

EUROPEAN DIESEL FUEL - A REVIEW OF CHANGES IN PRODUCT QUALITY 1986-1989

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Introduction

In Europe heavy goods vehicles are effectively 100% diesel engined. This coupled to the significant percentage of diesel powered passenger cars and light duty commercial vehicles results in Europe having the highest penetration of diesel engined vehicles worldwide (Fig 1). Despite the increasingly stringent emission limits and customer performance demands, technological advances by the diesel engine manufacturers are enabling them to keep up with such rapid change. Thus the position of the diesel engine appears secure in Europe, provided consistently high quality road diesel fuel is maintained.

The European refiner is facing a steady increase in demand for road diesel together with a decline in heating/off road gas oil volumes (Fig 2) due to competition from gas and other forms of energy. This is putting pressure on refiners to include greater proportions of cracked gas oils in the road diesel pool with the potential for stability problems - a major area of shortcoming for conversion distillate streams.

Gas Oil/Diesel Demand W. Europe
(1980 - 1995)

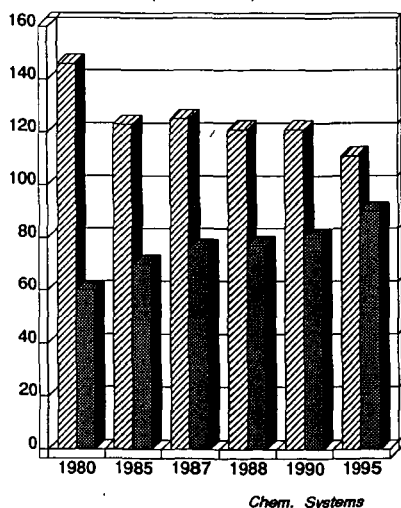


Fig. 2

Gas Oil Road Diesel

1080

Engine Production 1986

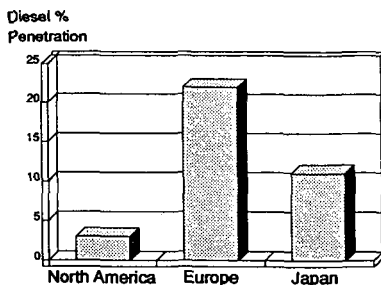


Fig. 1

This paper reviews the results of systematic winter surveys of road diesel fuel in Europe carried out from 1986-89 in which oxidative and thermal stability were evaluated along with other key parameters of diesel fuel quality.

Diesel Fuel Specifications

In Europe unleaded gasoline is unique in having a common specification from country to country. The national diesel fuel specifications detailed in Appendix 1 follow no set pattern with the exception of low temperature properties. These are consistent with the demands of geography. This lack of commonality of quality is a major concern to trans European operators of diesel vehicles. Likewise only the UK contains any stability standard and that a somewhat relaxed 2.5 mg/100 ml maximum in the ASTM D2274.

From the 1986-89 Ethyl diesel fuel surveys (Refs 1-3 and Appendix 2) consideration will only be given to the following primary diesel fuel properties

- 1) Density
- 2) Cetane Number
- 3) Cetane Index
- 4) Viscosity
- 5) Sulphur Content
- 6) Aromatics Content
- 7) Olefin Content
- 8) Oxidative Stability
- 9) Thermal Stability

Of these cetane number, oxidative stability and thermal stability can be improved by use of a suitable multifunctional diesel fuel additive package. The other primary features are purely influenced by refinery processing.

Density

The density of a diesel fuel affects the mass of fuel entering the combustion chamber and thus impacts on engine power, fuel economy and emissions.

The average density across Europe is essentially unchanged over the 3 years (Table 1). Even when individual countries are considered there is little annual variation. Austria is the only exception where density has risen steadily with time (Fig 3). This is coupled to a 17°C increase in the 50% distillation point and a smaller increase in end-point indicating a change in demand balance (Appendix 2).

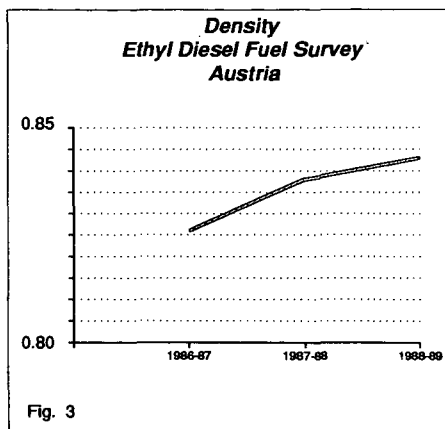


Fig. 3

Ethyl European Diesel Fuel Winter Survey Overall Mean Values

<i>Table 1</i>	1986-87	1987-88	1988-89
Density @ 15°C (g/cm ³) ASTM D4052	0.8380	0.8388	0.8368
Cetane Number, ASTM D613	51.3	51	52.5
Cetane Index, ASTM D976	51.2	50.4	51.3
Viscosity @ 20°C, ASTM D445	4.36	4.22	3.99
Sulphur, % weight, ASTM D4294	0.24	0.27	0.24
Aromatics, % vol ASTM D1319	29.2	32.1	26.9
Olefins, % vol ASTM D1319	0.6	1.6	3.8
Oxid. Stability, mg/100 ml, ASTM D2274	1.3	1.0	0.6
Pad Test, Rating	12*	7.5	5
*only 10 results.			

Cetane Number

Cetane Number is a measure of fuel ignition delay. This we consider to be the time between start of fuel injection and the rapid rise in pressure in the pre-chamber. Many other definitions are sometimes used (Ref 4).

Cetane number defines the ease of auto-ignition of the fuel. Whilst this is generally a reflection of the inherent stability of the molecules in a fuel, ignition improvers are often included to enhance performance.

Despite all the predictions of declining cetane quality due to increasing demand the overall picture in Europe is the reverse (Table 1). This is due to the introduction of premium quality diesel fuels containing multifunctional additives which can include cetane improver. This is most dramatically seen in West Germany (Fig 4) where premium diesel fuel was introduced in 1987 in response to OEM demands for higher quality fuels to reduce environmental emissions. As we discuss the other parameters the impact of this quality enhancement of diesel fuels will be further evidenced.

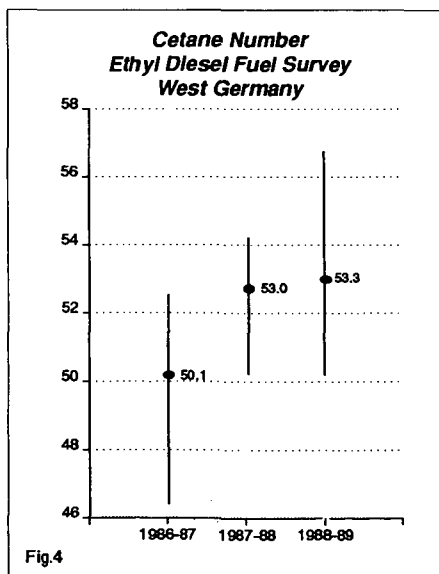


Fig.4

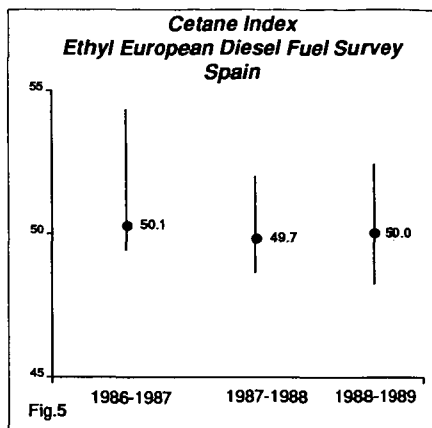


Fig.5

Cetane Index

This is an attempt to empirically predict a fuels ignition quality based on its density and boiling range. As this shows reasonable agreement with a fuels natural cetane it is arguably a better indicator of the European cetane pool than cetane number. And indeed this is unchanged across the 3 year period. However in Spain (Fig 5) both demand and refinery conversion is increasing whilst crude slate has resulted in lower natural indices and numbers. Thus cetane index has fallen steadily despite cetane number remaining high due to legislation of a 50 Cetane Number minimum but a 45 Cetane Index minimum thereby allowing refiners greater flexibility.

Viscosity

Viscosity variations have similar effects to those described for density. Additionally at low viscosities, below about 3 cSt @ 20°C, pumping leakage is increased with hot re-starts becoming difficult under hot ambient conditions, reduced power output and pump lubrication becoming critical. The combination of wide viscosity band variations with wide density variations exacerbates emission levels and vehicle performance.

Ethyl European Diesel Fuel Survey - Winter 1988/89

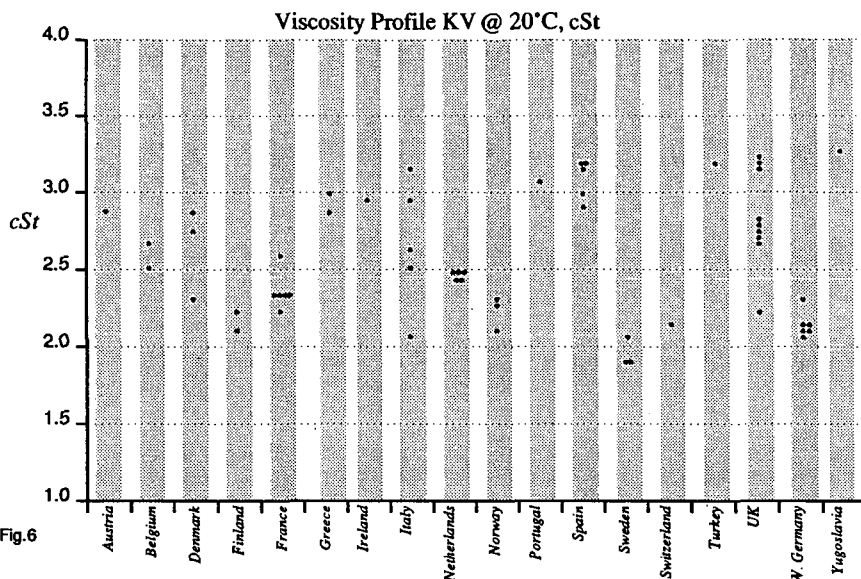


Fig. 6

There is some evidence (Table 1) for a general lightening of diesel fuel in Europe as a consequence of lower Cloud points. We do not see wide viscosity variations in Europe (Fig 6) and it is important to note this parameter is not a constraint since it is controlled indirectly by other diesel fuel properties such as Cloud Point, Density and Distillation range.

Sulphur Content

Worldwide concerns about "acid-rain" have resulted in legislation designed to control acidic emissions, most notably oxides of sulphur. Additionally the need for low sulphur fuel for satisfactory operation of low emissions oxidation catalyst equipped diesel vehicles is supporting this drive. The Californian standard of 0.05% max weight is the level that OEM's are requiring. In Europe the typical limit of 0.30% weight has moved down to 0.20% weight in the more environmentally sensitive countries. A good example of this is to contrast the sulphur contents in Italy and West Germany (Fig 7). This is placing increasing pressure on available refinery hydrotreating capacity and penalising higher sulphur crudes.

Aromatics Content

Aromatics, have been considered in certain studies to relate to deleterious emissions, particularly particulates. Several studies (Ref 5) claim to show links between the aromatics content of a diesel fuel and exhaust particulate emissions. Consideration is being

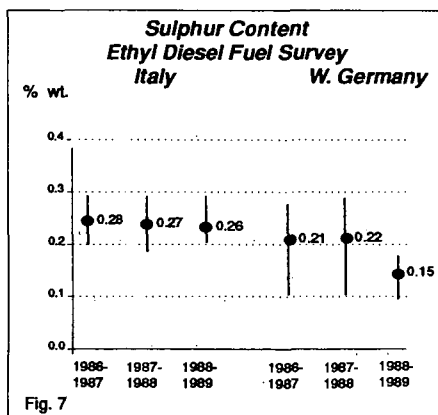
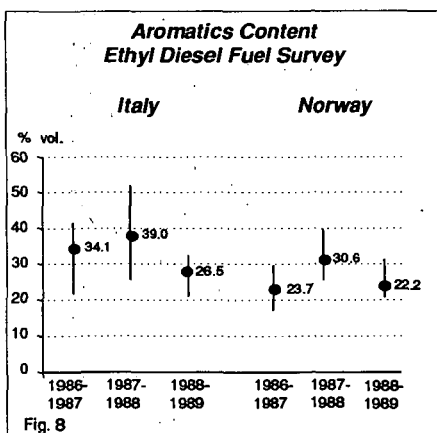


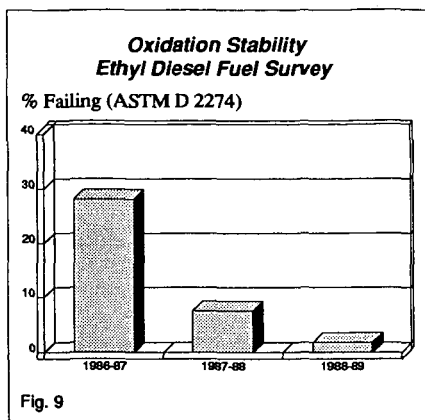
Fig. 7

given within the European Economic Community to follow the US example and limit the aromatics level of road diesel. Also being investigated is the best method for measuring the aromatics as the F.I.A. Method (ASTM D1319) often gives poor separation with heavier boiling European fuels (85% @ 350°C min is the common European limit). Whilst Table 1 would suggest there might be some overall decrease in aromatics levels in Europe it varies significantly country to country. Thus the high degree of conversion stream usage and heavier crude processing/higher distillation range is reflected in the high aromatics levels in Italy versus those of Norway (Fig 8), particularly pre-1988-89.



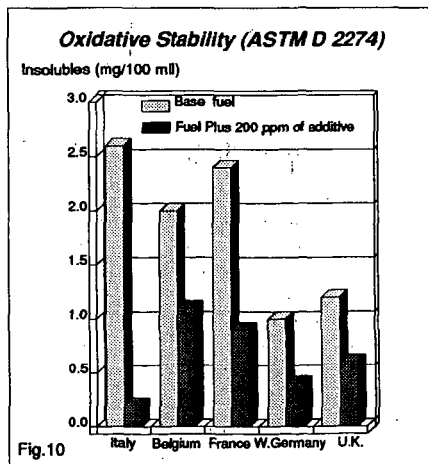
Olefin Content

Olefin levels in diesel are generally low however in terms of fuel stability they are regularly cited (Ref 6) as significant. It is thus interesting to note that every year from 1986 to 1989 the overall olefin level has doubled in Europe although the total percentage remains very small. Again this reflects the increasing use of conversion streams and level of hydrotreatment.



Oxidation Stability

Oxidation stability is widely considered to be an important parameter in determining the long term storage stability of a fuel. It is typically evaluated using the ASTM D2274 test developed by the US Navy. The limit for satisfactory field performance is usually taken as 1.5 mg/100 ml of insolubles. Figure 9 shows that the percentage of fuels with deposit levels above 1.5 mg/100 ml has fallen to negligible



Oxidation Stability v Thermal Stability Ethyl Diesel Fuel Survey 1988/89

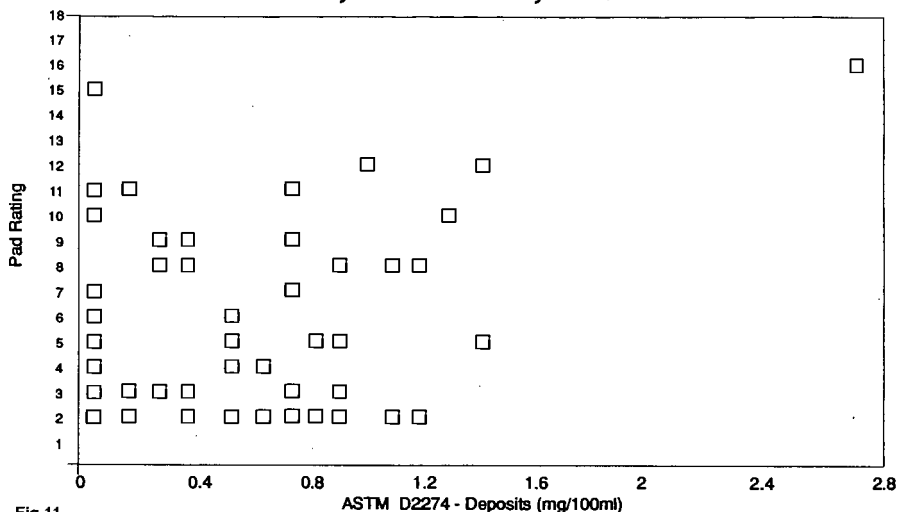


Fig.11

levels. This is thought to be due to the increasing use of multifunctional additive packages offering stability enhancement. An example of their effect is shown in Fig 10. This may also help explain the lack of an obvious relationship between thermal and oxidative stability (Fig 11).

Thermal Stability

Thermal stability whilst important in determining a fuels long term storage stability has also been linked to nozzle coking tendency (Ref 7). It is usually measured by some form of rapid thermal shock test followed by filtration and assessment of the filter deposits. Using the Ethyl Pad Procedure; where a rating of 20 is a black filter, 0 is clean and 7 is the maximum for good field performance we have observed results from 2 to 20 in our surveys. Previous work has suggested possible correlation with nozzle coking tendency, (Ref 8), surveys.

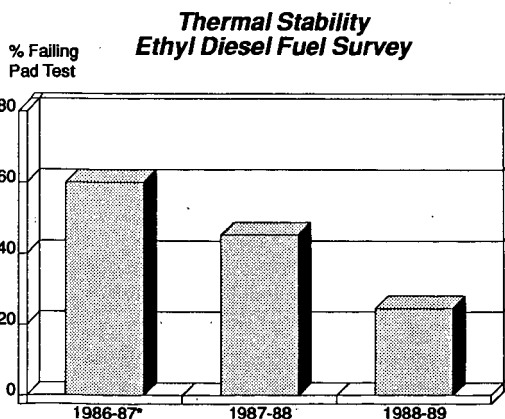


Fig.12 * (limited data-base)

Just as for oxidation stability the percentage of samples with ratings above 7 has declined steadily from 1986-89 (Fig 12). This is also surprising when viewed against the background of increasing olefin levels. Again the use of multifunctional additive packages is improving fuel stability. This also tallies with the poor agreement between olefin content and Pad Rating (Fig 13).

***Olefin Content v Thermal Stability
Ethyl Diesel Fuel Survey 1988/89***

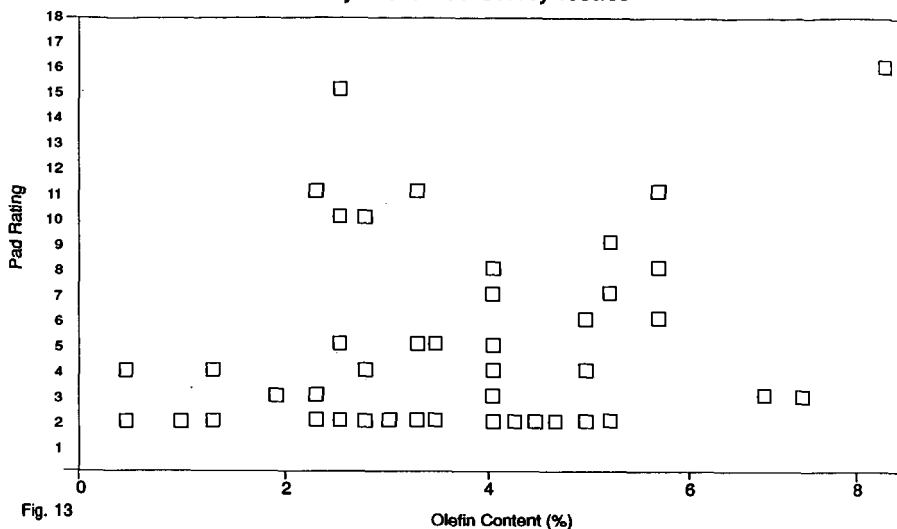


Fig. 13

Conclusions

The data reported in this paper indicate:

- 1) Diesel fuel quality remains high in Europe due in part to the increasing use of multifunctional diesel fuel additive packages
- 2) As a result of these marketing factors cetane number is increasing.
- 3) Sulphur levels are declining throughout Europe.
- 4) Olefin levels are increasing.
- 5) Oxidative and thermal stability are improving overall in Europe primarily due to the use of multifunctional diesel fuel additive packages.

References

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- 2) Ethyl European Diesel Fuel Survey Winter 1987-88
- 3) Ethyl European Diesel Fuel Survey Winter 1988-89
- 4) H.A. Henein and J.A. Bolt; SAE 67007
- 5) E.G. Barry and L.J. McCabe, D.H. Gerke and J.M. Perez; SAE 852078
- 6) M.W. Schrepfer, R.J. Arnold and C.A. Stansky, Oil and Gas Journal, January 16, 1984
- 7) M. Fortmagel and B. Herrbrich, API, New Orleans, 1984
- 8) P.B. Mabley and G.M. Wallace, Third International Stability and Handling of Liquid Fuels Conference, London, 1988

European National Specifications For Diesel Fuel

Country	Spec. Ref.	Density Kg/l	Distill., °C	KV @ 20°C, cSt	FL Pt., °C	CLP ₁ , °C	CFPP, °C	Pour Pt., °C	Sulphur, % Wt.	Cetane Index	Cetane Number
Austria	Ö Norm C1104	0.820-0.860	Min 85% @ 350	3.0 - 8.0	56 min	-	-15 - -22 max (W)	-	0.15 max	-	48 min
Belgium	NBN T32-713	0.820-0.870	Max 65% @ 250 Min 85% @ 350	4.0 max @ 40°C	56 min	-	-15 max (W)	-	0.2 max	-	46 min
France	CSR 05-M	0.810-0.890	Max 65% @ 250 Min 85% @ 350	9.5 max	55-120	-5 max (W) -8 max (W)* *Grand Froid	-15 max (W) -18 max (W)* *Grand Froid	-18 max (W) -21 max (W)* *Grand Froid	0.3 max	-	48 min
Greece	734/AB/86	Report	Min 85% @ 350 Max FBP @ 370 Athens	2 - 6 @ 37.8°C	55 min	-	-5 max (W) -2 max Athens (W)	-9 max (W) -6 max Athens (W)	0.3 max	47 min Athens 45 min Rest	-
Ireland	1.8.251:1981	0.825 min	Min 85% @ 350 Max FBP @ 380	2.0 min. @ 40°C	61 min	-2 max (W)	-12 max (W)	-	0.3 max	50 min	50 min
Italy	NCK30-01	0.8050-865	Max 65% @ 250 Min 85% @ 350	2.0-5.33 @ 37.8°C	55 min	-	-10 max (W)	-6 max (W)	0.3 max 0.2 max (cides)	48 min	47 min
Portugal	124/89	0.815-0.865	Max 65% @ 250 Min 85% @ 350	1.8-5.5 @ 40°C	56 min	-	-6 max (W)	-	0.3 max	45 min	-
Spain	Decree 1485/1987	0.825-0.860	Max 65% @ 250 Min 90% @ 350 Max FBP @ 380	4.5 max @ 37.8°C (W)	55 min	-1 max (W)	-8 max (W)	-	0.3 max	45 min	50 min
Sweden	S315 S432	0.800-0.860	Min 10% @ 230 Min 90% @ 360	1.5-4.0 @ 40°C	40 min	-10 max (W)	-20 max (W)	-	0.3 max 0.2 mean	45 min	45 min
Switzerland	SN181160/1	0.815-0.845	Min 90% @ 360	2.5 - 6.0	55 min	-6 max (W)	-15 max (W)	-15 max (W)	0.2 max	48 min	48 min
Turkey	TSE	0.850 max	Min 90% @ 363 FBP 391 max	1.0-6.0 @ 37.8°C	52 min	-	-	Report	1.0 max	50 * min *Diesel Index	-
U.K.	BS 2869	0.835-0.865	Min 50% @ 310 Min 85% @ 350	2.5-5.0 @ 40°C	56 min	-	-15 max (W)	-	0.3 max	46 min	48 min
W. Germany	DIN 51601	0.820-0.860	Max 65% @ 250 Min 85% @ 350	2.0 - 8.0	56 min	-	-15 max (W)	-	0.2 max	-	45 min
Yugoslavia	JUS B.312.410	0.810-0.860	Min 90% @ 360	1.8-9.0	55 min	-	-9 max (W)	-	1.0 max	-	45 min

N. B. (W) is Winter

Ethyl European Diesel Fuel Survey

Winter 1988/89

ASTM D1298	ASTM D445	ASTM D1319	ASTM D4294	ASTM D1319	ASTM D2274	Pad Test	ASTM D976	ASTM D613
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Greece

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
013	0.8423	5.19	32.1	0.4	0.48	2.0	16	52.8	51.2
014	0.8371	4.66	29.6	0.4	0.32	2.0	17	52.8	53.8

Italy

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
015	0.8472	5.39	41.5	0.4	0.28	1.8	16	52.3	50.6
016	0.8180	3.03	21.5	0.2	0.26	1.4	-	54.7	53.8
017	0.8493	5.20	41.1	0.4	0.27	2.0	5	50.2	49.4
018	0.8450	5.49	41.9	0.4	0.29	1.8	4	52.9	52.0
019	0.8262	3.98	24.7	0.5	0.30	1.4	-	56.5	55.5

Netherlands

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
020	0.8337	3.90	26.5	0.4	0.23	0.8	-	54.4	53.7
021	0.8283	3.75	25.9	0.4	0.17	-	53.1	54.1	-
022	0.8264	3.93	23.0	0.4	0.23	0.8	-	55.1	54.4
023	0.8313	3.47	33.1	0.4	0.07	1.2	-	50.8	51.4
024	0.8456	4.22	26.7	0.4	0.18	1.2	-	45.1	45.3

Norway

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
025	0.8336	3.34	28.8	0.5	0.29	1.2	-	50.9	49.2
026	0.8247	2.69	19.5	0.5	0.10	1.0	-	47.8	49.0
027	0.8276	3.19	22.9	0.4	0.10	1.0	-	50.5	50.4

Portugal

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
028	0.8438	7.02	33.8	0.4	0.46	1.6	-	54.2	54.6

Spain

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
029	0.8491	4.80	36.7	0.4	0.31	2.8	18	49.2	49.6
030	0.8290	4.16	25.4	0.4	4.16	3.4	3	54.4	53.9
031	0.8447	5.20	27.9	0.4	0.38	0.8	-	51.6	52.4
032	0.8483	4.94	28.9	0.4	0.35	1.6	-	49.2	50.0

Sweden

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
033	0.8338	4.04	27.9	0.4	0.16	1.3	-	53.1	53.8
034	0.8305	3.10	22.0	0.4	0.19	0.8	-	48.5	49.0
035	0.8352	3.47	24.3	0.4	0.23	1.5	-	49.5	49.4

United Kingdom

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	s% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
036	0.8438	4.77	27.7	0.4	0.15	2.4	-	50.9	51.9
037	0.8476	4.98	29.2	0.4	0.23	0.8	-	50.1	50.1
038	0.8457	4.74	28.8	0.4	0.09	0.8	-	50.4	50.9
039	0.8484	5.67	31.8	0.4	0.20	0.8	-	52.5	53.6
040	0.8370	4.44	28.2	0.4	0.19	2.3	11	52.2	52.2
041	0.8449	5.00	30.0	1.9	0.18	0.8	-	52.2	52.6
042	0.8412	4.73	28.4	0.4	0.21	1.5	-	52.5	53.6
043	0.8494	5.64	31.0	0.4	0.27	1.0	-	50.9	50.7
044	0.8428	4.51	30.0	0.4	0.22	0.8	-	50.2	50.5

W. Germany

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
045	0.8336	3.83	25.5	0.4	0.13	0.8	-	50.8	50.6
046	0.8392	3.84	29.6	0.4	0.24	0.8	-	46.8	46.7
047	0.8292	3.65	21.8	0.4	0.19	1.0	-	54.6	52.7
048	0.8273	3.63	21.3	0.4	0.25	2.0	20	52.8	51.3
049	0.8350	3.44	25.9	0.4	0.28	0.8	-	47.9	46.6
050	0.8259	3.35	21.6	0.4	0.17	0.8	-	51.7	52.9

Ethyl Diesel Fuel Survey Winter 1987/88

ASTM D1298 ASTM D445 ASTM D1319 ASTM D4294 ASTM D1319 ASTM D2274 Pad Test ASTM D976 ASTM D613

Austria

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
001	0.8377	4.09	27.8	1.3	0.17	0.9	4	49.7	49.1

Belgium

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
002	0.8390	4.38	36.2	0.9	0.21	0.9	9	51.7	51.7
003	0.8463	4.40	34.1	2.7	0.25	0.9	7	48.7	48.6

Denmark

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
004	0.8392	4.01	28.1	4.3	0.20	0.8	3	50.2	56.7
1092	0.8565	5.06	39.3	1.5	0.17	0.8	14	47.2	44.9

Finland

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
006	0.8380	3.33	32.7	2.0	0.11	0.7	14	46.4	49.6
007	0.8397	3.34	34.3	1.8	0.13	1.2	46.3	49.8	

France

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
008	0.8335	3.48	30.3	0.4	0.28	0.9	7	50.0	48.5
009	0.8374	3.83	30.3	0.5	0.33	0.8	10	50.1	49.0
010	0.8287	3.83	26.5	0.7	0.26	0.9	10	54.3	51.6
011	0.8308	3.58	25.9	0.8	0.23	0.9	2	51.4	52.3
012	0.8395	4.35	32.5	1.3	0.32	0.7	8	51.4	50.4
013	0.8328	3.86	29.0	1.0	0.31	0.9	7	50.7	48.9

Greece

Code No.	Density	KV @ 20 °C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
014	0.8426	4.84	32.8	2.3	0.50	1.2	16	51.9	50.9
015	0.8418	5.87	33.7	0.8	0.29	0.8	3	54.7	53.5

Italy

Code No.	Density	KV @ 20 °C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
016	0.8415	4.82	39.1	1.3	0.25	4.3	14	51.9	49.3
017	0.8272	2.97	27.0	4.8	0.19	0.9	15	49.1	48.1
018	0.8499	5.62	52.1	4.8	0.30	0.9	14	51.7	48.7
019	0.8461	4.45	44.1	1.8	0.30	2.3	14	48.9	50.9
020	0.8362	5.20	32.8	0.8	0.29	2.6	14	55.4	55.7

Netherlands

Code No.	Density	KV @ 20 °C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
021	0.8474	4.32	34.4	1.1	0.27	1.0	2	49.9	51.4
022	0.8365	3.93	28.2	1.0	0.21	0.8	2	51.3	49.9
023	0.8281	4.15	30.1	3.8	0.26	0.8	3	53.4	52.9
024	0.8355	3.77	29.7	2.9	0.21	0.9	2	51.0	49.8
025	0.8403	4.17	32.7	2.2	0.28	0.9	3	50.7	53.1

Norway

Code No.	Density	KV @ 20 °C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
026	0.8454	3.80	31.4	1.6	0.17	0.8	6	46.7	47.0
027	0.8300	3.23	26.5	0.9	0.19	0.9	3	49.4	50.7
028	0.8384	3.56	34.0	0.6	0.13	0.8	7	49.0	48.9

Portugal

Code No.	Density	KV @ 20 °C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
029	0.8411	5.55	34.0	0.6	0.46	0.9	7	53.6	54.6

Spain

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
030	0.8555	5.43	38.5	0.7	0.50	0.9	1	47.9	51.2
031	0.8411	4.54	35.8	2.1	0.49	1.2	1	51.2	52.4
032	0.8466	5.21	36.5	1.8	0.42	0.9	-	50.8	50.7
033	0.8590	5.80	49.8	2.1	0.42	0.7	-	48.8	47.2

Sweden

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
034	0.8282	3.22	25.6	1.0	0.19	0.8	8	50.6	52.0
035	0.8285	2.89	24.7	1.0	0.12	0.9	19	46.6	50.9
036	0.8411	3.50	33.6	1.1	0.19	0.8	14	46.9	48.8

Switzerland

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
037	0.8297	3.35	26.2	1.0	0.16	0.7	10	51.1	49.9

United Kingdom

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
038	0.8467	5.58	39.8	1.1	0.19	0.9	3	51.9	49.1
039	0.8494	4.54	35.9	0.7	0.22	1.8	12	48.3	49.6
040	0.8461	4.38	33.6	1.2	0.05	0.8	5	48.9	48.7
041	0.8510	5.55	38.6	1.5	0.23	0.9	2	51.3	50.9
042	0.8497	4.97	36.8	0.6	0.20	0.9	14	50.9	51.2
043	0.8434	4.82	29.6	1.4	0.23	0.8	3	51.5	51.7
044	0.8483	4.30	34.3	1.3	0.15	0.9	1	49.6	50.8
045	0.8418	4.41	31.3	1.3	0.24	0.8	5	52.0	50.1
046	0.8467	5.58	40.6	3.2	0.20	0.8	8	52.9	54.1

Germany									
Code No.	Density	KV @ 20 °C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
047	0.8302	3.35	26.5	1.2	0.13	0.8	3	47.4	51.9
048	0.8337	3.54	32.8	1.4	0.26	0.8	3	49.4	50.1
049	0.8215	3.27	23.2	1.0	0.27	0.8	2	52.5	54.4
050	0.8232	3.34	23.7	1.6	0.26	0.9	3	50.8	54.0
051	0.8286	3.11	26.8	0.6	0.29	0.9	10	48.0	54.1
052	0.8287	3.25	26.2	1.9	0.13	0.7	3	49.1	53.5

Yugoslavia									
Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxide. Stab	Thermal Stab	CI	CN
053	0.8338	4.27	29.1	1.5	0.65	0.9	3	52.7	53.6

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Austria

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
001	0.8426	4.42	29.7	4.6	0.14	0.8	2	50.5	53.8

Belgium

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
002	0.8429	4.51	32.5	5.6	0.17	0.5	6	51.4	50.6
003	0.8402	4.22	28.5	4.3	0.23	0.7	7	52.7	49.2

Denmark

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
004	0.8461	4.37	22.6	4.1	0.18	0.5	5	49.1	49.4
005	0.8437	4.21	26.6	1.5	0.17	0.6	4	50.2	48
006	0.8222	3.37	21.8	1.8	0.20	0.8	5	53.6	53.2

Finland

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
007	0.8379	3.30	30.3	0.7	0.07	0.4	2	47.2	50.1
008	0.8384	3.46	31.9	0.9	0.08	0.8	4	48.1	51

France

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
009	0.8365	3.91	28.4	4.4	0.26	0.1	4	53.0	51.7
010	0.8318	3.41	23.0	2.8	0.32	0.1	10	52.0	53.4
011	0.8346	3.80	28.0	3.6	0.19	0.4	3	52.8	51.8
012	0.8289	3.69	26.1	3.6	0.15	0.2	11	52.8	51.8
013	0.8276	3.59	21.0	5.4	0.35	0.6	2	54.7	54.7
014	0.8321	3.47	22.8	5.3	0.30	0.1	7	52.6	51.1

Greece

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxide, Stab	Thermal Stab	CI	CN
015	0.8482	5.35	32.4	4.3	0.48	0.9	8	51.5	56.9
016	0.8278	4.50	17.8	3.8	0.21	1.5	12	57.1	56.9

Ireland

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxide, Stab	Thermal Stab	CI	CN
017	0.8493	4.49	31.7	4.0	0.17	1.3	10	50.3	52.7

Italy

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxide, Stab	Thermal Stab	CI	CN
018	0.8413	4.64	32.4	3.3	0.26	1.1	2	52.2	52.6
019	0.8255	3.64	20.8	8.4	0.25	2.7	16	55.0	53.1
020	0.8358	4.60	27.5	7.0	0.24	0.9	3	54.6	54.7
021	0.8289	3.91	21.7	5.3	0.26	0.7	9	55.7	55.3
022	0.8379	3.92	30.0	3.7	0.30	1.0	12	52.1	54.2

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Netherlands

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxide, Stab	Thermal Stab	CI	CN
023	0.8362	3.76	25.1	4.1	0.20	0.7	3	52.1	52.8
024	0.8268	3.63	22.5	3.1	0.16	0.5	2	54.3	52.9
025	0.8234	3.67	22.2	5.1	0.16	0.1	4	56.0	55.4
026	0.8368	3.54	31.0	4.4	0.14	0.9	3	52.3	52.2
027	0.8375	4.18	24.8	4.7	0.19	0.2	2	51.6	52.2

Norway

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxide, Stab	Thermal Stab	CI	CN
028	0.8351	3.45	23.1	2.9	0.12	0.4	2	50.2	51.5
029	0.8283	3.15	20.8	2.6	0.10	0.8	2	47.8	51.6
030	0.8355	3.11	22.8	3.4	0.10	0.1	2	48.0	50.6

Portugal

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
031	0.8379	5.51	28.6	4.4	0.49	0.2	2	54.6	56.9

Spain

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
032	0.8429	4.77	26.2	2.8	0.41	0.1	2	51.0	54.3
033	0.8509	5.16	36.2	3.6	0.44	0.2	3	50.7	51.6
034	0.8567	4.98	33.5	5.7	0.45	0.7	11	47.5	53.9
035	0.8514	5.01	38.0	3.8	0.52	0.9	5	49.4	51.6
036	0.8463	5.30	35.6	5.0	0.44	1.2	2	51.6	52.8

Sweden

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
037	0.8257	2.70	23.2	1.1	0.12	0.7	2	46.0	46.5
038	0.8295	3.15	26.8	1.1	0.09	0.6	2	48.0	48.8
039	0.8239	2.85	22.5	1.5	0.17	0.7	2	48.2	47.9

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Switzerland

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
040	0.8281	3.18	19.7	5.1	0.11	0.1	6	50.6	52.7

Turkey

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
041	0.8391	4.27	26.6	3.7	0.72	0.4	3	53.7	53.7

United Kingdom

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxida. Stab	Thermal Stab	CI	CN
042	0.8462	4.39	28.3	3.5	0.16	0.1	5	51.1	51.8
043	0.8408	4.21	28.1	3.1	0.18	0.5	4	48.7	51
044	0.8506	4.16	32.3	4.0	0.06	0.3	9	47.9	52.2
045	0.8453	4.52	27.7	4.5	0.20	0.1	2	51.6	53.3

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United Kingdom (continued)

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
046	0.8473	4.42	31.4	3.9	0.17	50.2	49.6	55.4	54.3
047	0.8337	4.50	24.6	2.9	0.18	0.1	15	52.7	55.4
048	0.8403	4.18	27.5	3.8	0.16	0.1	3	51.3	55.3
049	0.8455	4.58	33.3	2.6	0.25	0.1	11	49.4	51.6
050	0.8453	4.34	32.4	3.5	0.17	0.1			

West Germany

Code No.	Density	KV @ 20°C	% Aromatics	% Olefins	% Sulphur	Oxidn. Stab	Thermal Stab	CI	CN
051	0.8285	3.24	23.2	4.1	0.12	0.9	2	50.8	56.8
052	0.8238	3.02	19.7	4.4	0.17	0.1	3	49.7	52.4
053	0.8244	3.06	23.3	2.5	0.16	0.3	3	49.2	54.5
054	0.8232	3.01	19.7	6.8	0.16	0.2	3	49.4	53.1
055	0.8371	3.39	31.2	2.9	0.17	1.5	5	47.2	50.2
056	0.8287	3.45	20.3	4.0	0.10	0.3	3	51.4	53.1

Yugoslavia

Code No.	057
Density	0.8440
KV @ 20°C	4.64
% Aromatics	31.8
% Olefins	5.7
% Sulphur	0.90
Oxidn. Stab	0.5
Thermal Stab	8
CI	56.3
CN	53.6

THE CHEMISTRY OF SEDIMENT FORMATION IN AUSTRALIAN MIDDLE DISTILLATE FUELS

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Introduction

In earlier publications it was suggested that the formation of insolubles during storage of an unstable UK middle distillate fuel was caused at least in part by reactions of the chemical species indoles, phenalenes and acids^{1,2}. The purpose of this present study was to determine whether reactions involving these species contributed to the storage instability of middle distillate fuels from quite different sources and to investigate the extent of correlation between fuel chemical composition and observed fuel storage stability.

The reaction sequence previously proposed is illustrated schematically in figure 1. The oxidation of phenalene and its alkyl homologues to the corresponding phenalenone species has been shown to occur both in model systems and in middle distillate fuels containing light cycle oils. The formation of indolylphenalenes, indolylphenalenones and 'indolylphenalene/acid salts' by acid promoted reactions of indoles and phenalenones has also been demonstrated by the isolation of these species both from model systems and from unstable fuel containing light cycle oil^{3,4,5}. The role of acid in these reactions is not clearly understood. However it is known that at least catalytic amounts of acid are required for indoles to react with phenalenones and there is some evidence to suggest that acids become incorporated into the most polar components of insoluble fuel degradation products⁶.

The significance of this chemistry with respect to the stability of middle distillate fuels produced in Australian refineries has been investigated. The concentrations of phenalenone and alkylindoles were determined before and after storage of fuel samples for 13 weeks at 43C. Insoluble fuel degradation products were analysed by thin layer chromatography and compared with insolubles formed by degradation of fuels from UK sources.

Experimental

Fuel samples were supplied directly from Australian oil refineries and generally consisted of one of five refinery stream types; straight run distillate (SRD), light cycle oil (LCO), hydrotreated light cycle oil (HT-LCO), hydrotreatment unit feed (LCO/SRD) or hydrotreatment unit product (HT-LCO/SRD). The samples from each refinery were combined to produce 12 blends containing 70% straight run distillate and 30% cracked components. The blend compositions are listed in table 1. Aliquots of both blended and unblended components were stored at -12C to minimise degradation before testing and analysis.

The stability of the blends was assessed by storage of 1 litre aliquots of fuel at 43C for 13 weeks, following the method detailed in ASTM D4625. Tests were carried out in duplicate. Filterable insolubles were determined using glass fibre filters (Millipore AP40). Adherent insolubles were determined by hotplate evaporation of gum solvent washings contained in disposable aluminium dishes. The chemical nature of insolubles formed during the storage tests was assessed using thin layer chromatography (silica gel stationary phase, 10% methanol in dichloromethane mobile phase). The concentration of phenalenone was determined using normal phase HPLC with UV detection at 384nm. The

detection limit for phenalenone was 0.5 $\mu\text{mol/l}$ with repeatability of $\pm 10\%$. The relative concentrations and distributions of alkylindoles were determined by a procedure which involved fractionation of fuel samples over silica gel, followed by addition of an internal standard (1-methylindole) and finally GC analysis with nitrogen specific detection.

GC peaks corresponding to alkylindoles were identified by reference to the published literature^{8,9}. The relative concentration of alkylindoles in the fuel blends was calculated by assuming an equal detector response for all isomers and homologues. This method can also be used to determine the distribution and concentration of carbazole and its alkyl homologues.

Results and Discussion

The stability of the 12 fuel blends was assessed by storage at 43°C for 13 weeks. This test is widely believed to provide a realistic acceleration of degradation processes which occur at temperatures typically encountered in fuel storage facilities¹⁰. The relatively mild test conditions are considered to be approximately equivalent to one year of fuel storage at 18°C to 24°C. The results of this test are given in table 1. The filterable and adherent insolubles, produced during the storage period by all but the most stable fuels (samples 8,10,12,14), were analysed by thin layer chromatography and compared with insolubles produced during storage of unstable UK fuel. The isolation and characterisation of the UK insolubles has been described previously^{11,12}. The chromatographic characteristics of the UK and Australian insolubles (both filterable and adherent) were found to be very similar. Subtle differences were noted amongst the most polar sediment components, but the degree of variation was within that previously observed for insolubles from different UK sources. Whilst not conclusive in itself, the similar characteristics of these fuel degradation products provided a positive indication that they may have been formed by common chemical processes.

The effect of chemical composition on observed fuel stability was addressed specifically in terms of the concentration of species highlighted in figure 1. According to this reaction scheme, unstable fuels would be expected to initially contain both phenalenes and indoles, with the concentration of phenalenes, indolylphenalenes and further reaction products (including insolubles) increasing with time. The acidic species required to promote these reactions may be present initially or may be produced during fuel storage. Stable fuels would be characterised by the absence of one or more of these chemical species.

In order to test this line of reasoning, specific chemical analysis was carried out on the fuel blends before and after thermal stress. The initial presence and subsequent reduction in concentration of phenalenes could have been determined in one of two ways; either directly, using reversed phase HPLC with electrochemical detection⁷, or indirectly by determination of increasing phenalenone concentration using normal phase HPLC with UV detection. For simplicity of analysis, the latter approach was adopted in this study, with measurements being carried out before storage, after storage for 16 hours at 100°C (to provide an initial indication of phenalene/phenalenone content) and after storage for 13 weeks at 43°C. The results quoted in table 2 relate only to the concentration of the single species phenalenone. The total concentration of phenalenone species (alkyl- and benz- derivatives) in the fuels samples would of course have been higher. In addition it should be noted that the measured concentration of phenalenone was consistently lower than the initial concentration of phenalene. Previous work has shown that phenalene is not quantitatively converted to phenalenone⁷. The total concentration of alkylindoles was determined in a limited number of the fuel samples before and after the 13 week storage test. The results of these measurements are given in

table 3. The remaining key species highlighted in the reaction scheme, namely acids, were not determined in this study.

The results of the storage tests, given in table 1, showed that the fuels tested covered a wide range of stability.

Four fuels (samples 8,10,12,14) proved to be extremely stable, all producing less than 1mg/l of total insolubles and not darkening in colour beyond 1.5 ASTM D1500 colour units. None of these fuels formed significant quantities of phenalenone during storage, indicating the virtual if not complete absence of phenalene species. The concentrations of alkylindoles in two of these samples were determined. Sample 8 initially contained alkylindoles at a concentration equivalent to 0.19mmols of 1-methylindole, and no significant reduction in concentration was observed during the storage period. The concentration of alkylindoles in sample 10 was an order of magnitude lower than in sample 8, essentially at the detection limit of the method. Again no significant change in concentration was detected during the storage period. The behaviour of these fuels was therefore entirely consistent with the reaction scheme illustrated in figure 1, ie. stable fuels characterised by the absence of one or more of the key reactive species, phenalenes in the case of sample 8 and both phenalenes and indoles in the case of sample 10.

The four very stable fuels (8,10,12,14) all contained hydrotreated light cycle oil blending components. The beneficial effect of hydrotreatment on fuel stability is well known. This improvement in stability on hydrotreatment was clearly shown by the storage test results for the matched fuel pairs 7/8, 9/10, 11/12 and 13/14, where in each case the first sample contained light cycle oil and the second sample contained hydrotreated light cycle oil. The effect of hydrotreatment on the chemical composition of the fuel samples was also consistent with the observed improvement in stability. All the light cycle oil samples produced phenalenone during thermal stress, indicating the initial presence of phenalene species. However these species were removed during hydrotreatment to produce the stable 'phenalene free' fuels discussed previously. The effect of hydrotreatment on the initial alkylindole concentration was found to be variable. The light cycle oil samples all contained alkylindoles. There was no significant reduction in the initial concentration after hydrotreatment for sample pair 7/8, but a 25 fold reduction was noted for sample pair 9/10, indicating the use of much more severe hydrotreatment conditions.

The remaining fuel which contained hydrotreated light cycle oil was sample 16. Despite the hydrotreatment, this fuel was found to be moderately unstable, producing about 8mg/l total insolubles and darkening significantly in colour during the storage period. It produced low but significant levels of phenalenone during storage, thus indicating the initial presence of phenalene species. The alkylindole content of this fuel was not determined. However it is reasonable to assume that alkylindoles were present, since high levels of alkylindoles were detected in fuel containing light cycle oil from the same refinery (sample 15) and it is unlikely that hydrotreatment conditions which left low levels of phenalene species would significantly reduce the concentration of alkylindoles. In addition, the insolubles produced during degradation of both samples 15 and 16 were clearly shown by ILC to be of the same type as those produced by fuels thought to follow the chemistry outlined in figure 1, which of course requires the presence of alkylindoles.

Other fuels which were found to be of similar stability to sample 16, producing 5 to 12mg/l total insolubles, were samples 6, 7 and 13. All these fuels contained light cycle oil and initially contained alkylindoles and phenalene species. The initial concentration of alkylindoles in sample 13 could not be measured because the fuel contained a high level of 'unidentified' nitrogen compounds which co-eluted and effectively masked the presence of alkylindoles. This was the only sample examined which contained these compounds. Further work is required in order to identify these species and investigate their

significance. The initial presence of phenalene species in samples 6, 7, 13 and 16 was indicated by formation of significant amounts of phenalenone (more than $5\mu\text{mol/l}$) after storage of the fuels at 100°C for 16 hours with the measured level increasing further during the 13 week storage period. The amount of phenalenone present at the end of the 13 week storage test ranged from $10\mu\text{mol/l}$ for sample 16 to $230\mu\text{mol/l}$ for sample 6. This variation, which presumably also reflected differences in initial phenalenes concentration, clearly demonstrated that the degree of fuel instability cannot necessarily be extrapolated simply from the level of phenalene species. Indeed it is also worthwhile noting that the quantity of phenalene species and alkylindole species estimated to be present in fuel insolubles was always small in comparison to amounts potentially available in fuel solution. For example sample 15 produced approximately 56mg/l of sediment but at the end of the storage period it still contained about 95mg/l alkylindoles and 35mg/l phenalenone (total phenalenes concentration would be several times this level). This observation tended to support previous conclusions that, given the presence of indoles and phenalenes, the amount of insolubles formed during storage is limited by acid concentration.

The fuels which proved to be the most unstable during the 13 week storage period were samples 5, 9, 11 (each producing about 18mg/l total insolubles) and sample 15 (producing about 56mg/l total insolubles). Chemical analysis of these samples indicated the presence of comparatively high levels of phenalene species and alkylindoles, consistent with their observed instability. Examination of the individual SRD and LCO components used in blending of samples 5, 9 and 15 showed as expected that phenalene species and alkylindoles originated entirely from the LCO components.

Significant reductions, $>0.05\text{mmol/l}$, in the overall concentration of alkylindoles were noted for the unstable fuel samples 5, 6, 7, 9 and 15 (concentration changes for the other two unstable fuels, samples 11 and 13 were not determined), thus providing strong evidence for reaction of alkylindoles during fuel storage. These changes represented reductions of between about 20% and 60% of the total initial alkylindoles concentration. The largest proportionate decrease was noted for the most unstable fuel, sample 15, and the smallest decrease for the most stable of these fuels, sample 7. Detailed examination of chromatograms showing the distribution of indoles in these aged fuel samples revealed that in all cases the concentration of certain isomers and homologues had decreased more than others. Figure 2 shows the chromatographic distribution of alkylindoles in sample 15 before and after aging. Very similar profiles were obtained for samples 5, 6, 7 and 9. Dorbon and Bernasconi have also recently noted that the distribution of alkylindoles in light cycle oils changes during aging at 43°C . In all cases the decrease in alkylindoles concentration during aging was greater than the quantity of these species estimated to have been incorporated into the insolubles collected at the end of the storage period. The amount of alkylindoles unaccounted for ranged from 3 to 10 times the amount estimated to be contained in the insolubles. The shortfall was probably associated with involatile but soluble fuel degradation products, such as for example the 'sediment precursor' compounds, indolylphenalenes, referred to in previous publications^{1,2}. Soluble fuel degradation products of this type almost certainly contribute to 'fuel soluble gum' which may lead to deposits on hot engine and fuel system components.

Summary and Conclusions

The thin layer chromatographic characteristics of insolubles formed during storage of unstable middle distillate fuels from Australian refineries were found to be very similar to those of insolubles produced by the degradation of unstable fuel from UK sources, indicating that they may have been formed by similar chemical processes. All fuels which subsequently proved to be unstable during storage initially contained both alkylindole and phenalene species. Stable fuels were characterised by the absence of one or both of these

compound types. Phenalenes were either removed entirely or their concentration significantly reduced by hydrotreatment, which had the expected effect of improving fuel stability. In one case the initial concentration of alkylindoles was significantly reduced by hydrotreatment, but in all other cases no concentration change was noted. The reactivity of alkylindoles in unstable fuels was demonstrated by reductions in their overall concentration during fuel storage. In line with previous reports⁷, the distribution of alkylindole isomers and homologues was observed to change during fuel storage, indicating differences in reactivity amongst the species. Whilst the results of this study show that the absolute amount of insolubles formed during a storage period cannot be correlated directly with the concentration of alkylindole and phenalene species, it is clear that the stable fuels were characterised by the absence of one or both of these species and that both species were present in all the unstable fuels. These results therefore illustrate the potential for application of chemical methods to differentiate between stable and unstable fuels. However other factors clearly need to be considered when assessing the degree of fuel instability. From a chemical viewpoint, fuel acidity and fuel acidity potential are known to be important. Further work is required to identify the nature of acids in middle distillate fuels and to clarify their role in fuel degradation. In addition, physical parameters such as the solubility of fuel degradation products also need to be considered, particularly when fuel stability is assessed simply in terms of the weight of insolubles formed during fuel storage.

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Table 1. Results of fuel storage at 43 C for 13 weeks

Sample number	Sample type *	Initial colour	Final colour	Filtered insolubles mg/l	Adherent insolubles mg/l	Total insolubles mg/l
5	A(i)	0.5	4.0	9.9	8.0	17.9
		0.5	4.0	10.7	7.1	17.8
6	8(i)	1.0	4.5	4.7	7.0	11.7
		1.0	4.5	4.6	7.2	11.8
7	B(iii)	1.0	3.0	3.9	1.8	5.7
		1.0	3.0	3.0	1.9	4.9
8	B(iv)	0.5	<1.5	<0.1	0.1	0.1
		0.5	<1.5	0.3	0.4	0.7
9	C(i)a	<1.0	4.5	9.8	8.6	18.4
		<1.0	4.5	9.7	9.9	19.6
10	C(ii)a	0.0	0.5	0.2	0.2	0.4
		0.0	0.5	0.3	0.5	0.8
11	C(i)b	<1.0	<4.0	3.8	14.8	18.6
		<1.0	<4.0	2.5	15.0	17.5
12	C(ii)b	0.0	<0.5	0.8	<0.1	0.8
		0.0	<0.5	0.2	0.6	0.8
13	D(i)	<1.0	<3.0	2.0	7.4	9.4
		<1.0	<3.0	0.8	7.8	8.6
14	D(ii)	1.0	<1.5	1.0	<0.1	1.0
		1.0	<1.5	0.6	<0.1	0.6
15	E(i)	1.5	<7.5	23.4	33.2	56.6
		1.5	<7.5	23.4	32.4	55.8
16	E(ii)	2.5	<4.5	2.5	4.9	7.4
		2.5	<4.5	3.3	5.0	8.3

- X Refinery Code
- (i) 30% LCO in SRD
- (ii) 30% HT-LCO in SRD
- (iii) 30% LCO/SRD in SRD
- (iv) 30% HT-LCO/SRD in SRD

Table 2. Results of phenalenone measurements

Sample number	Phenalenone content $\mu\text{mol/l}$		
	(A) Initial	(B) After 16hrs @ 100 C	(C) After 13wks @ 43 C
5	4.4	42.0	150.1
6	12.7	87.8	230.8
7	6.1	30.7	52.6
8	ND	3.2	2.2
9	8.9	44.2	175.2
10	ND	2.0	ND
11	9.4	37.9	162.3
12	ND	ND	ND
13	ND	6.6	48.8
14	ND	ND	ND
15	15.6	107.2	193.8
16	ND	8.1	10.7

ND = not detected

Table 3. Results of indoles measurements

Sample number	Total indole content (mmol/l equivalent of 1-methylindole)		
	• (A) Initial	(B) After 13wks @ 43 C	($\bar{A} - \bar{B}$)
5	0.32	0.18 \pm 0.02	0.14 \pm 0.02
6	0.70 \pm 0.05	0.39 \pm 0.01	0.31 \pm 0.06
7	0.23 \pm 0.01	0.18 \pm 0.00	0.05 \pm 0.01
8	0.19 \pm 0.05	0.17	insignificant
9	0.50 \pm 0.02	0.25 \pm 0.01	0.25 \pm 0.03
10	0.02 \pm 0.01	0.01 \pm 0.00	insignificant
13	**	0.06 \pm 0.00	
15	1.25 \pm 0.02	0.52 \pm 0.03	0.73 \pm 0.05

* Average of duplicate results

** Initial alkylindole concentration could not be determined because of interference from 'unidentified' nitrogen compounds

Figure 1. SEQUENCE OF REACTIONS LEADING TO DIESEL FUEL DEGRADATION

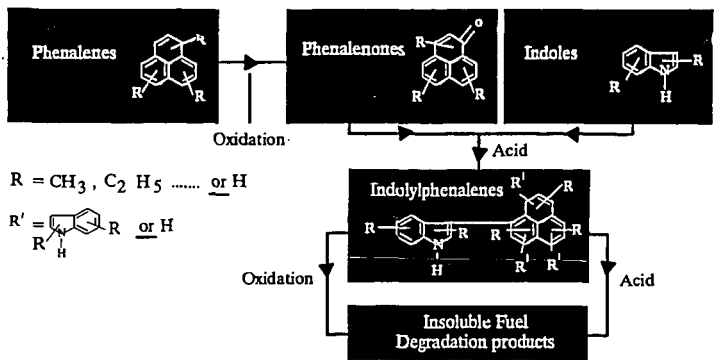
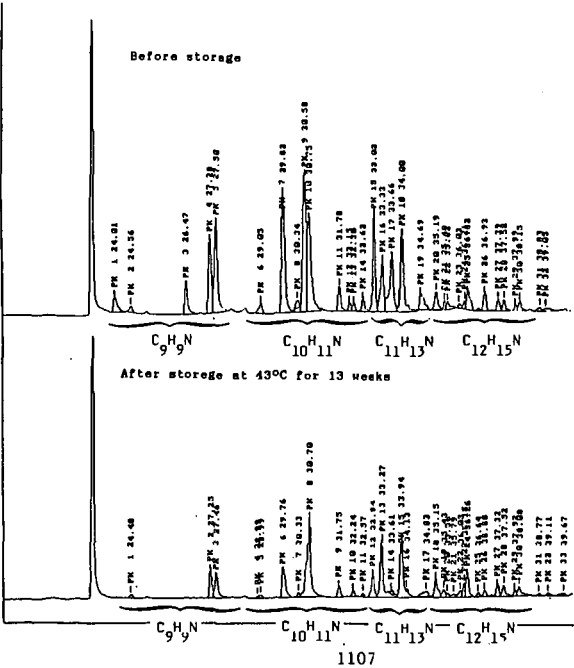


Figure 2. Chromatographic distribution of indoles in fuel sample 15.
GC conditions: 30°C to 280°C at 4°C per minute



STORAGE STABILITY OF DISTILLATE DIESEL FUELS: CHANGES IN PHENALENE AND PHENALENONE CONCENTRATIONS DURING LONG TERM AMBIENT STORAGE

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INTRODUCTION

Unstable distillate fuels can degrade during storage forming insoluble sediment and darkening in colour. Pedley, Hiley and Hancock^{1,2} have proposed a reaction mechanism to account for the production of the majority of the sediment, in which indoles react with phenalenones to form soluble sediment precursors (indolylphenalenes and indolylphenalenones) which in turn react with acids to form sediment. The chemistry is complex; a simplified mechanism is shown in Figure 1.

Methods of analysis have been developed to quantify phenalenes and phenalenones directly in fuels to low ppm levels^{3,4}. Application of these methods to a number of fuels has shown that phenalenes and phenalenones are not present in stable straight run fuels, but are present in a number of cracked fuels. The total concentration of phenalenes and phenalenones may be as high as 0.1%, although blends containing cracked stocks generally exhibit much lower concentrations.

Previous trials⁵ have shown that the phenalenes content of an unstable catalytically cracked stock diminished from approximately 0.1% to zero over a period of a year, while the phenalenones content increased. From these trials it became apparent that neither the phenalenes/phenalenones nor indoles contents were necessarily the limiting factors in sediment production. However the trials gave no information on the rate of depletion of the phenalenes, the rate of increase of the phenalenones or the relationship of the concentrations of these species to the production of sediment.

This paper describes the changes in phenalene and phenalenone concentrations of an unstable fuel blend with time, and examines any correlation between these concentrations, sediment levels and colour.

EXPERIMENTAL

A research blend consisting of 50% fresh catalytically cracked gas oil and 50% fresh straight run gas oil (both from North Sea crude stocks) was subjected to long term storage at ambient temperatures in 50 litre vented non-lacquer lined mild steel drums, and sub-sampled for compositional data.

The stability of the blend was assessed initially using ASTM D2274, ASTM D525/D381 modified (16 hours at 100°C in oxygen), an in-house method (3 days at 80°C) and also using ASTM D4625 (storage for 16 weeks at 43°C). The sediment in the latter tests was measured at 4 weekly intervals.

The phenalenes and phenalenones concentrations of the blend were monitored using chromatographic methods^{3,4}. The phenalenes were determined using reverse phase HPLC with electrochemical detection to selectively quantify the phenalene species. Phenalenones were measured using normal phase HPLC selectively detecting these compounds by UV absorbance at 400nm. Filterable sediment levels and colour (ASTM D1500) were also monitored at intervals.

RESULTS AND DISCUSSION

Accelerated storage tests.

Results from the ASTM D2274 tests imply that the fuel blend was stable, with <0.1 mg/100ml total insolubles formed during the ageing period (Table 1). Similar results were obtained from the in-house method (3 days at 80°C). Very high levels of gum were predicted by ASTM D525/D381. These tests were therefore considered unsuitable for predicting storage stability. The results of the ASTM D4625 test indicate that the fuel produced <2 mg/100ml insolubles during the first four week period but thereafter there was a rapid increase to about 12 mg/100ml after 16 weeks (Fig 2, Table 1).

Ambient storage

Filtered sediment

There appears to have been an induction period of between 16 and 20 weeks during which sediment formation was less than 2mg/100ml. Thereafter there was a rapid increase in sediment in the fuel, rising to about 17mg/100ml after 50 weeks storage (Fig 3, Table 2).

An attempt was made to relate the sediment formed in the ambient drum storage to levels predicted in the ASTM D4625 tests. It has been assumed that 1 week at 43°C is equivalent to 4 weeks storage under ambient conditions. The data show (Table 2) that within the precision of the test procedures, there is some correlation, particularly up to 40 weeks storage. Thereafter, sediment increased at a faster rate in the drum storage and after 50 weeks storage, the level of sediment was greater by a factor of 2 over predicted levels. Although absolute levels of sediment were not predicted accurately, the figures indicated the overall likely stability of the blend.

Phenalenenes concentration changes

The initial concentration of phenalenenes (phenalene and its alkyl homologues) in the untreated blend was high at 850 mg l^{-1} . The phenalenenes concentrations diminished with time and were still present at about 100 mg l^{-1} after one year's storage (Table 3, Figure 4). The results indicate that the oxidation of the phenalenenes approximates to a pseudo-first order reaction in the fuel (Figure 5). This conclusion should be treated with caution, however, as the exact mechanism of phenalene oxidation has not yet been established. The phenalenyl radical has been observed in diesel fuels^{1,12} and is probably involved in the reaction mechanism in hydrocarbon fuels. It has not yet been established whether phenalenones are produced directly from the radical, or whether further intermediates, such as the hydroxyphenalenenes, could also be involved. Phenalenenes are also produced as a byproduct of the condensation reaction producing indolylphenalenenes and indolylphenalenones⁸, thus continually modifying the phenalenenes concentration with time. The related compound benzantracene was initially present at 100 mg l^{-1} (the homologues of this compound were not quantified), and although not quantified throughout the storage period, appeared to diminish in a similar way to the phenalenenes.

The phenalene homologues exhibited a similar distribution to that seen in other fuels containing 'fresh' catalytically cracked stock, namely that the major constituents were the monomethylphenalenenes (about 50% of the initial total phenalene content), followed by the dimethyl or ethyl substituted phenalenenes, at about 40%. Phenalene itself comprised only a small proportion of the total phenalene content - approximately 12% (Table 3).

Phenalenones concentration changes

The phenalenones concentrations were initially low at 15mg l^{-1} total phenalenones, with phenalene itself the major constituent (Table 4). The general pattern of phenalenones distribution previously observed in other fuels was noted in this blend and was consistent throughout the storage period: phenalene as the major constituent, approximately 40% of the total phenalenones concentration, followed by the 2-, 5-, and 8-methyl derivatives at about 30% to 50% of the phenalene concentration, and the remaining methyl homologues at low concentrations. The concentration of 9-methylphenalene remained at trace levels only, 2mg l^{-1} being the highest concentration recorded. The dimethyl or ethylphenalenones and higher homologues were not quantified. However, there are no large peaks in the phenalene chromatogram unaccounted for. It may therefore be reasonably assumed that unless the dimethyl homologues have considerably lower absorbances at 400nm than phenalene, these compounds are not a major proportion of the total phenalenones found in fuels. The related benzantrones were present at all times at considerably lower concentrations than the phenalenones (Table 4), with benzantrone the major constituent.

There appeared to be an induction period of two to three weeks where the ketones concentrations remained static, after which the concentrations gradually increased. After about 13 weeks the total phenalenones concentrations increased markedly before beginning to plateau out (Figure 6). The benzantrones acted in a similar fashion. It is interesting to note that the concentration of 2-methylphenalene was initially very similar to that of the 5- and 8-methyl homologues, but with time the 2-methylphenalene content increased at a faster rate than its isomers (Figure 7). After a year the concentration of the 2-methylphenalene was approximately double that of the 5- and 8-substituted isomers. This reflects model compound studies⁹ where 2-methylphenalene was found not to react with indoles in acid conditions.

The concentrations of phenalene and the methylphenalenones always appeared less than the initial concentrations of phenalene and monomethylphenalenones respectively. As with previous model studies⁹, the mass balance for the phenalene species is difficult to reconcile, only approximately 50% of the initial phenalenones being accounted for from the measurement of phenalene, phenalenones and sediment (estimating the contribution from phenalene species in the sediment to be about 35% of the mass). Known products include phenalenones, indolylphenalenones and indolylphenalenones, and salts of these products which comprise a large proportion of the sediment. Phenalenones¹¹ may also be produced during the reaction with indoles which would in part account for the discrepancy.

Colour and sediment changes

The data indicate a gradual deterioration in colour during the first 20 weeks of storage followed by a period of little change (Table 2, Figure 8). There appears to be a correlation between colour and phenalenones concentrations. The relationship appears to be linear from the available data (Figure 9). The increase in concentration of the coloured ketones with time would contribute to the darkening of fuel during storage and to the formation of the fuel-soluble sediment precursors. The darkening in colour is believed to be more attributable to the formation of the latter and it would be informative to quantify the precursors for this reason.

The relationship between sediment levels and phenalenones concentration is demonstrated in Figure 10. The relationship appears to be linear for this fuel blend, with a sharp change in gradient when the total phenalenones concentration reaches approximately 130mg l^{-1} - equivalent to about thirteen weeks storage. A similar correlation is obtained between sediment levels and the concentration of phenalenones excluding those substituted in the 2-position. The relationship follows the same pattern as for total phenalenones, and there is a sharp change in gradient at about 100mg l^{-1} phenalenones - again, equivalent to about thirteen weeks storage.

Studies of previous trials^{4,6} have shown that the strong acid content of fuels starts to increase after similar periods of storage and it is possible that increased production of strong acids such as aromatic sulphonic acids will enhance the rate of sediment production. The initial thiol content of the fuel was low (0.0007% m mercaptan sulphur) and the fuel blend contained negligible strong acid (<0.05mg KOH.l⁻¹ by conductometric titration⁶) throughout the storage trial. The concentrations of indoles and phenalenes/phenalenones were very high and it might be expected that the strong acids appeared to be entirely consumed in the production of sediment (Figure 1), indicating that the acidity of the fuel was the limiting factor in the sediment forming process for this fuel.

CONCLUSIONS

There was no correlation between results from accelerated ageing tests at high elevated temperature and levels of sediment produced during natural ageing. Reasonable correlation was obtained with results by ASTM D4625, ageing for 16 weeks at 43°C.

Phenalenes appeared to deplete by a pseudo- first order reaction at ambient temperatures. The reaction possibly proceeds via radical formation but further details of the mechanism are not known ie whether intermediates such as the hydroxyphenalene are produced. The order of reaction obtained should be treated with caution as phenalenes may also be produced as byproducts from the phenalene/indole condensation reaction. The concentrations of the phenalenes and the benzanthrone increased with time to a plateau. The concentration of 2-methylphenalene reached higher concentrations than the 5- and 8-methylphenalenes, consistent with model studies showing that this compound does not react with indoles.

Colour and sediment levels appear to follow the same trend as phenalene concentration. There appear to be direct correlations between the colour and sediment produced and the concentration of phenalenes for this fuel blend. More fuels from different sources should be examined to confirm this. The limiting factor in sediment formation for this fuel appeared to be the acidity of the fuel, in particular the availability of strong acids.

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TABLE 1 - RESULTS OF ACCELERATED AGEING TESTS

Analysis	Week	Result	Analysis	Week	Result
Filtered Sediment			ASTM D4625		
GFC Paper	0	0.1	Filterable Insolubles mg/100ml	0	<0.1
Colour ASTM D1500	0	<3	Adherent Insolubles mg/100ml	0	<0.1
			Total Insolubles mg/100ml	0	<0.1
ASTM D2274			Filterable Insolubles mg/100ml	4	0.7
Filtered Insolubles mg/100ml	0	<0.1	Adherent Insolubles mg/100ml	4	0.3
Adherent Insolubles mg/100ml	0	<0.1	Total Insolubles mg/100ml	4	1.0
Total Insolubles mg/100ml	0	<0.1	Filterable Insolubles mg/100ml	8	2.8
ASTM D525 (modified)			Adherent Insolubles mg/100ml	8	2.1
Potential gum	0	226	Total Insolubles mg/100ml	8	4.9
After heptane wash	0	225	Filterable Insolubles mg/100ml	12	1.8
Colour after ageing	0	4.5	Adherent Insolubles mg/100ml	12	6.1
			Total Insolubles mg/100ml	12	7.9
80°C STORAGE (MOD method)			Filterable Insolubles mg/100ml	16	4.0
Insolubles mg/l	0	2	Adherent Insolubles mg/100ml	16	6.9
			Total Insolubles mg/100ml	16	10.9

TABLE 2 - FILTERED SEDIMENT AND COLOUR MEASURED DURING AMBIENT STORAGE

Week no	Filtered Sediment Measured	mg/100ml Predicted	Colour ASTM D1500
0	1.1		<3.0
4	0.2		2.5
8	0.7		<4.0
12	1.1		4.0
16	1.1	1.0	5.5
20	2.5		5.5
24	4.7	3.0	5.5
28	7.5		5.5
32	6.6	4.9	6.0
36	10.9		6.0
40	9.2	6.4	6.0
50	16.8	8.3	7.0

TABLE 3 - CHANGES IN PHENALENES CONCENTRATIONS WITH TIME

Time wks	Phenylene mg l ⁻¹	C1 Phenalenes mg l ⁻¹	C2 Phenalenes mg l ⁻¹	Total Phenalenes mg l ⁻¹
1.5	115	445	300	860
2	105	395	250	750
8	65	245	140	450
13	70	220	100	390
18	75	350	170	595
24	55	230	135	420
30	35	150	75	260
36	30	115	55	200
40	20	60	30	110
46	20	75	40	135

TABLE 4 - CHANGES IN PHENALENONES CONCENTRATIONS WITH TIME

Time wks	Phenalenones concentrations in mg l ⁻¹								Total Phenalenones mg l ⁻¹	Total Benzanthrones mg l ⁻¹
	Phenalenone	2-Me	Phenalenone Homologues 3 & 4-Me 5-Me 6-Me				7-Me	8-Me	9-Me	
1.5	6	2.8	0.9	2.7	ND	ND	2.6	ND	15	0.2
2	6	3.4	0.9	3.2	0.1	0.4	3.0	ND	17	0.2
4	6	5.4	0.4	3.0	0.1	0.1	3.0	ND	19	0.2
6	15	8.5	4.0	6.0	1.6	1.0	4.0	0.3	40.5	4.0
8	15	14	3.0	7.0	1.0	2.0	6.5	0.3	49	8.0
13	34	30	3.0	16	3.6	2.0	15	0.3	104	10
18	49	31	6	21	5	3	19	1.5	135	20
24	64	35	4	14	3	2	25	1.5	149	24
28	64	38	6.5	17	4	5	25	1.5	161	20
36	84	53	9	27	6	4	32	2	217	35
40	70	50	4	23	3	3	25	1	179	22
46	75	60	3	23	1	1	24	1	188	24

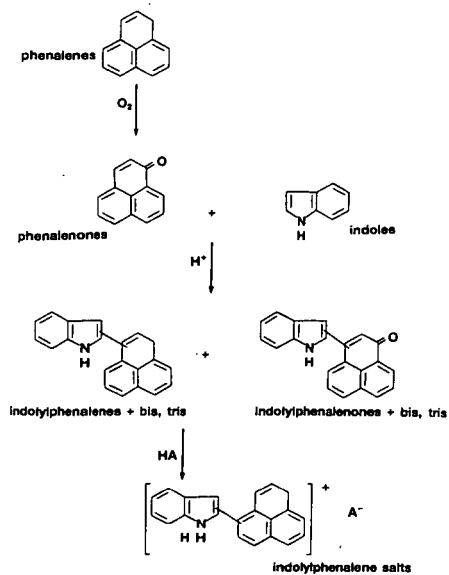


Figure 1. Reaction mechanism for sediment formation.

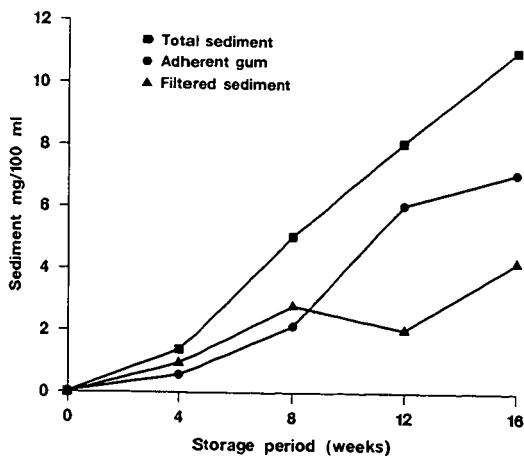


Figure 2. Changes in total sediment with time (bottle storage at 43°C).

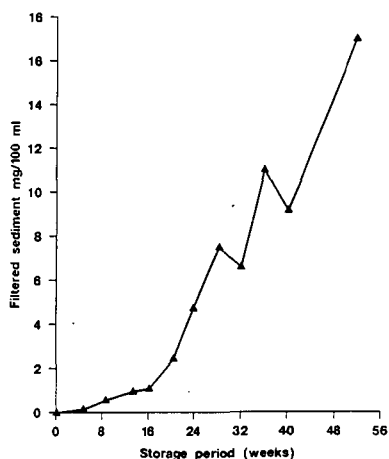


Figure 3. Changes in filtered sediment with time (drum storage).

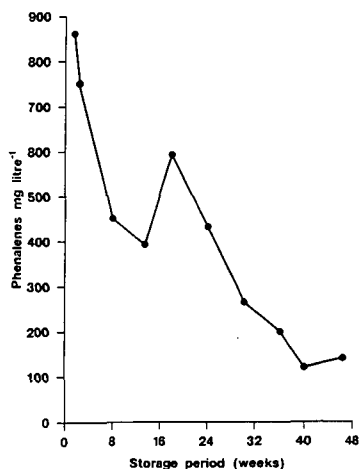


Figure 4. Changes in total phenalenes concentration with time (drum storage).

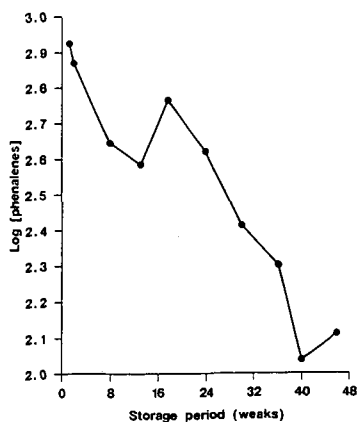


Figure 5. Changes in log [phenalenes] with time (drum storage).

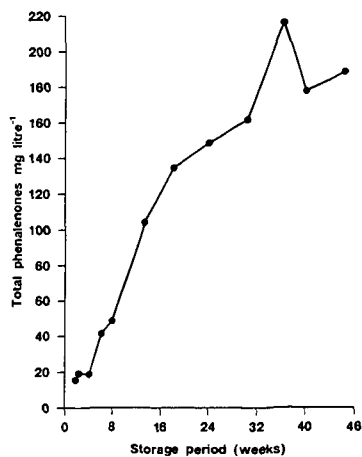


Figure 6. Changes in total phenalenones concentration with time (drum storage).

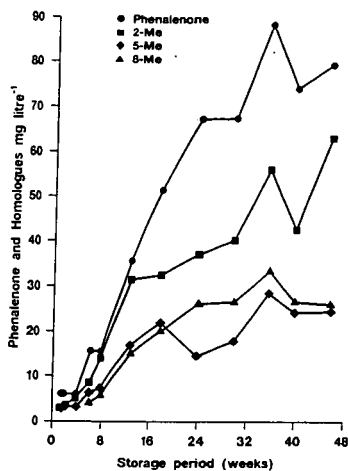


Figure 7. Changes in phenalenone and homologues concentrations with time (drum storage).

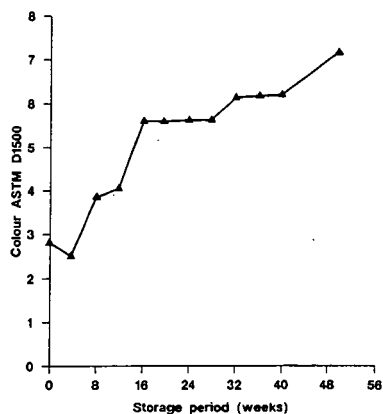


Figure 8. Changes in colour with time (drum storage).

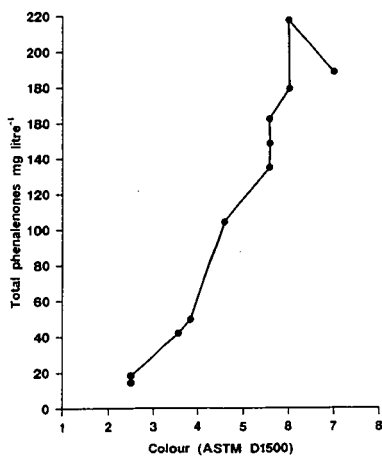


Figure 9. Changes in colour with total phenalenones concentration (drum storage).

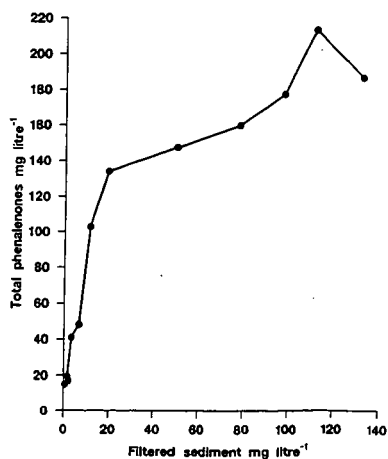


Figure 10. Changes in filtered sediment levels with total phenalenones concentration (drum storage).

Rates of Indole - Phenalenone Reactions in Middle Distillate Fuel

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ABSTRACT

Although reactions of indole species with phenalene species have been postulated as contributing to sediment formation upon ageing of distillate fuels, no evidence has been found for reaction of phenalenone species in accelerated ageing of fuels by the oxygen overpressure technique or higher temperature ageing. Most indole species, either from chemical sources or from methanol extracts of LCO (MELCO), were found to react under all experimental conditions, even in experiments in which no sediment was produced. Addition of either indole or 2-methylindole to MELCO/straight run distillate mixtures produced considerably more particulate matter on ageing, whereas no additional particulate was formed by addition of 3-methylindole. The results would support formation of indole/phenalene particulate in aged fuels by reaction of phenalene and alkyl substituted phenalenes with the 3-position of alkylindoles.

INTRODUCTION

Reactions between alkylindoles and phenalenones have been postulated to be a significant factor in the formation of sediments in middle distillate fuels.¹ Alkylindoles have also been reported to decrease in concentration during the ageing of fuel containing light cycle oil (LCO).² In studies of sediments formed from ageing of distillate fuels from Australian refineries,³ although species associated with reaction products of alkylindoles with phenalenone were identified in the sediments, in all cases the concentration of phenalenones increased in the ageing fuel mixture. The increases in the concentration of phenalenones is undoubtedly associated with the oxidation of phenalenes present in the LCO.⁴ However, as the concentration of phenalenones also increase in the ageing of fuels containing LCO, their specific role in sediment formation remains speculative.

This study was undertaken primarily to investigate the role of phenalenones in the formation of sediments. As a secondary objective, a limited study was also undertaken of the rates of reactions of alkylindoles. Two approaches were used for this investigation. The first was the addition of phenalenone, indole or methylindoles to blends of straight run distillate (SRD) or to 30% LCO/SRD blends followed by accelerated ageing of the mixture. Secondly, polar solvent extraction of LCO was undertaken as a means to separate the polar species containing heteroatoms from the less polar hydrocarbons. The extracts were then added to SRD as means of simulating the presence of LCO in SRD while minimizing the oxidation of phenalenes to phenalenones.

EXPERIMENTAL

Experimental fuel samples were obtained directly from automotive distillate streams of Australian refineries. Experiments in Table 1 were done with SRD from refinery A,³ while those in Table 3 were done with SRD from refinery G. They were stored at -12°C upon receipt from

the refinery, which was within one week of production. Immediately before being used for the experiments described in this presentation, the samples were thawed, blended and filtered through Millipore AP40 glass fibre filters. Pairs of these filters were used for sediment determination by the method of ASTM D4625. Sediment determination were done in duplicate for model compound additives and the average of the two results shown in the Table 1. Results in Table 3 are for single determinations only.

Commercial samples of indole, 2-methylindole and para-toluenesulphonic acid monohydrate from Fluka Chemika and 3-methylindole and phenalenone (perinaphthenone) from Aldrich Chemicals were used directly as received.

Polar extracts of LCO were obtained by shaking 500 ml of the LCO from refinery F³ with 5 x 100 ml portions of methanol. The methanol extracts were combined and stored at -12°C. Prior to ageing experiments, measured portions of the methanol extract were evaporated to dryness under vacuum at ambient temperature. The residue was then dissolved in the experimental fuel blend.

Most accelerated ageing studies were carried under oxygen overpressure conditions⁵ using the single bomb apparatus of ASTM D942 at a oxygen pressure of 794 kPa and temperature of 95°C as outlined elsewhere.⁶ These conditions for an ageing time of 64 hours will be referred to as OP conditions in the remainder of the paper. Studies were also carried out at atmospheric pressure in a thermostated air oven using 700 ml of fuel in loosely capped 1 litre borosilicate flasks.

Phenalenone and indole determinations were performed on the experimental fuel blends prior to and after fixed ageing periods. Determination of phenalenones was performed by high pressure liquid chromatography using a Waters 5 μ m spherical silica column of 150 mm length and 4.6 mm diameter at ambient temperature. All phenalenones were eluted under isocratic conditions with a 9:1 mixture of heptane with chloroform containing 1.5% propan-2-ol. Following elution of the phenalenones, the column was flushed with propan-2-ol prior to the next run. The phenalenones were detected by serial detectors at wavelengths of 384 nm and 254 nm. Good agreement was obtained between the two wavelengths after standardization with 0-1000 μ mol/L solutions of phenalenone in the eluent, indicating the minimal co-elution of interfering substance with the phenalenones. Indoles were determined by gas chromatography using a nitrogen specific detector as described elsewhere.⁶ Thin layer chromatography (TLC) of sediments were performed on Merck HPTLC Silica Gel 60 F254 plates using a 10% methanol/dichloromethane solvent.⁶

RESULTS AND DISCUSSION

Ageing of samples of SRD alone produces very little sediment, but upon admixture of LCO with the SRD, significant amounts of sediment are produced.⁷ Phenols⁸, phenalenones¹, alkylindoles^{1,2}, and acids^{7,9} have all been postulated to be precursors for sediment formation. A reference sample of SRD was aged for the equivalent of 3-5 years ambient ageing under the vigorous conditions of the oxygen overpressure test⁵ for 64 hours at 95°C with a pressure of 794 kPa oxygen. Both phenalenone and indole then were added to the SRD at concentrations of 588 μ mol/L and 981 μ mol/L respectively. These are equivalent to concentrations at the upper end of those measured for phenalenone and alkylindoles in 30% LCO/SRD blends.³ As may be seen from Table 1, no additional sediment was formed in the fuel containing the additives on ageing.

The results would also suggest that species which catalyse the reactions of indole with phenalenone are not formed from stressing of the SRD under the OP conditions. In particular,

the acid species which would be expected to be formed,⁹ do not act as a catalyst. In order to investigate the effect of strong acids further, a saturated solution at 20°C of para-toluenesulphonic acid monohydrate in SRD containing indole and phenalenone as previously was prepared and aged under the OP conditions. This acid is known to be effective in promoting sediment formation in fuel containing LCO.⁷ No additional sediment was formed compared to SRD without additives. It may be concluded that the concentration of p-toluenesulphonic acid dissolving at 20°C in combination with acid produced by OP ageing of the SRD is insufficient to promote reaction between the indole and phenalenone in the SRD.

The experiments were then repeated with a fuel mixture of 30% LCO in SRD. This mixture produced 67 mg/L sediment under the OP conditions without the addition of additives. Phenalenone and indole were added and the fuel aged. The amount of sediment increased to 125 mg/L. Phenalenone was then added to the 30% LCO/SRD fuel without any indole. The amount of sediment formed after OP ageing at 63 mg/L was the same within the experimental error as that produced from the reference 30% LCO/SRD blend. Finally, for these series of experiments shown in Table 1, indole without phenalenone was added to the reference fuel. The amount of sediment of 122 mg/L formed after OP ageing was the same as that produced for fuel containing both phenalenone and indole.

The effect of methyl substitution upon the indole nitrogen containing ring was then investigated. The addition of 2-methylindole to the 30% LCO/SRD fuel mixture produced 157 mg/L sediment after OP ageing, whereas the addition of 3-methylindole resulted in only 60 mg/L of sediment. Increased sediment is formed from 2-methylindole compared to indole itself, whereas 3-methylindole does not produce any additional sediment compared to the undoped fuel. These results would suggest that reaction of the indole molecule to form sediments is via the 3-position. The 2-methyl substituent facilitates reaction at the 3-position, whereas the 3-methyl group blocks the reaction.

The results may be compared with the effect upon sediment formation of the presence of both 3-methylindole and tert-butylhydroperoxide in shale derived fuels.¹⁰ Significantly increased sediment formation was observed when both additives were present. It may be concluded that sediment formation from 3-methylindole in the presence of tert-butoxy radicals is predominantly a free radical process. Hindered phenols act as effective free radical traps, but are known to be ineffective in reducing sediment formation in unstable fuels.¹¹ As no evidence was found for the reaction of the 3-methylindole under the OP conditions of this work, it may be concluded that the OP conditions are more comparable to ambient ageing than those in the presence of free radical promoters.

TLC analyses of the sediments were undertaken to compare sediments produced from the 30% LCO/SRD mixture in the presence and absence of additives. These are shown schematically in Table 2. Thin layer chromatograms of sediments from the reference fuel without additives, and from that containing either phenalenone or 3-methylindole were identical within experimental error, confirming that these additives had not contributed to the sediments. Only sediment from the reference fuel is shown in Table 2. The major feature of the thin layer chromatograms of sediment from the indole additive was the increased prominence of a blue material at approximate R_f 0.25 to 0.35. With the 2-methylindole additive this blue material was very intense. It is postulated to be the acid salts of alkyindolylphenalenes.

Direct measurements of indole concentrations were not done for the experiments in Table 1. Indole concentrations that are shown are those which were added to the solution. In a second series of experiments, direct measurements of indole concentrations were made before and after ageing. For these experiments shown in Table 3, methanol extracts of LCO

from refinery F were also added to SRD from refinery G. This combination was used due to the relatively high indole content of the LCO for refinery F³ and the water white nature of SRD from refinery G.

Ageing of the SRD under the OP conditions used previously produced 10 mg/L total particulate from the SRD. Similar ageing of the SRD with added indole, both with and without added phenalenone, produced the same amount of sediment as the SRD alone within the experimental error. The indole and phenalenone concentrations were measured in the solution after ageing as shown in Table 3. The final phenalenone concentration was unchanged from that initially and consistent with no additional sediment being formed in the presence of the phenalenone. However, although no additional sediment was formed in either solution in the presence of added indole, in both cases the concentration of indole had decreased to approximate half its original value. These results clearly indicate a non-particulate forming reaction of the indole in the SRD.

Ageing of SRD containing methanol extracts of LCO produced 89 mg/L of sediment. The addition of 490 $\mu\text{mol/L}$ of phenalenone to the solution prior to ageing did not produce any change in the amount of sediment formed. The results are comparable with those of Hardy and Welcher,¹² who found that ageing methanol extracts of LCO in hydrocarbons produced sediments of similar mass to that produced from the equivalent volume of unextracted LCO. As with the experiments discussed in the previous paragraph, the total indole concentration (in the case of the extract it is a mixture of many alkyl indoles⁹) decreased considerably in the aged solution, whereas the phenalenone concentration was unchanged after ageing.

The ageing of the methanol extract in SRD was repeated with an air atmosphere in an thermostated oven. Both the initial total alkylindole and phenalenone concentration was low at 270 and 4 $\mu\text{mol/L}$ respectively and only 6 mg/L of sediment was formed after 14 days ageing at 80°C. The addition of 780 $\mu\text{mol/L}$ of phenalenone to the reference solution resulted in the formation of 7 mg/L of sediment, unchanged within the experimental error. Again there was a significant reduction in the final total indole concentration, but none in the final phenalenone concentration. Finally, a greater concentration of methanol extract in SRD was aged with an air atmosphere for 65 hours at 120°C. After this period, 41 mg/L of sediment had been formed and the total alkylindole concentration had decreased to one fifth of its original value, but the phenalenone concentration was unchanged at 28 $\mu\text{mol/L}$. Not only was the unsubstituted phenalenone concentration unchanged after ageing at the elevated temperature, but so were all other substituted phenalenones as detected in the HPLC chromatogram at a detector wavelength of 384 nm as shown in the chromatograms before and ageing in Figure 1. Although these other species have not been definitively identified as phenalenones, the HPLC retention time and absorption at 384 nm is indicative of the phenalenone chromatophore.

If phenalenone species do not react with indoles in SRD under the severe ageing conditions used in this work, it may be concluded that it is unlikely that they react at ambient temperatures. However, blue and pink materials observed in the thin layer chromatograms of the sediments from this and previous work has been postulated to be acid salts of alkylindolylphenalenes and alkylindolylphenalenes.^{1,6} It is proposed that the acids salts arise following reactions between alkylindoles with unoxidized phenalene species to form indolylphenalenes which may subsequently oxidized to indolylphenalenes as shown in Figure 2. Phenalenes have been shown to be present in relatively high concentrations in LCO.⁴ The large increase in blue material observed in the thin layer chromatogram of sediment formed upon ageing when 2-methylindole is added to fuel mixture containing LCO follows from coupling with phenalenes at the favoured 3-position of the alkylindoles. This coupling is blocked in the case of 3-methylindole.

CONCLUSIONS

No evidence has been found for reaction of phenalenone species under conditions of oxygen overpressure and elevated temperature ageing of SRD containing either indole and phenalenone as model compounds or these species present from methanol extracts of LCO. Indole species were found to react under all the experimental ageing conditions. Although approximately 50% of indole in SRD aged under OP conditions of 64 hours at 95°C was found to have reacted, no additional particulate matter was formed in the fuel.

Particulate matter was formed on ageing when solid residue from methanol extracts of LCO were added to SRD. The total alkylindole concentration in the SRD/extract mixture decreased by at least 50% during the ageing experiments. However, in none of the experiments was any decrease in phenalenone concentration recorded. No additional particulate matter was formed when phenalenone was added to SRD/extract mixture.

Addition of either indole or 2-methylindole to the extract/SRD mixture resulted in considerably more particulate matter being produced. No increase in particulate was found when the SRD/extract mixture containing 3-methylindole was similarly aged.

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FUEL	INDOLE ADDED umol/L	PHENALENONE ADDED umol/L	TOTAL PARTICULATE mg/L
SRD	0	0	17
SRD	981	588	14
30% LCO/SRD	0	0	67
30% LCO/SRD	793	604	125
30% LCO/SRD	0	627	63
30% LCO/SRD	972	0	122
30% LCO/SRD	754 ^a	0	157
30% LCO/SRD	792 ^b	0	60

^a as 2-methylindole
^b as 3-methylindole

Table 1. Total sediment formed after oxygen overpressure ageing at 794 kPa for 64 hours at 95°C of fuel from Refinery A.

R _f RANGE	BAND COLOUR	NO ADDITIVES	INDOLE ADDED	2-METHYLINDOLE ADDED
1.00-0.96	green	L	L	L
0.94-0.87	orange	L	M	D
0.74-0.73	green	VL	NO	VL
0.72-0.71	grey	VL	NO	VL
0.55-0.43	pink	M	L	M
0.42-0.26	blue	L	D	VD
0.26-0.22	orange	VL	M	NO
0.21-0.25	yellow	NO	M	NO
0.08-0.04	brown	L	M	M

NO not observed
VL very light
L light
M medium
D dark
VD very dark

Table 2. Thin layer chromatogram schematics of sediment from 30% LCO/SRD fuel from refinery A.

Fuel Ageing	TOTAL ALKYLINDOLE concentration		PHENALENONE concentration		TOTAL PARTICULATE MATTER mg/L
	Initial umol/L	Final umol/L	Initial umol/L	Final umol/L	
a	0	0	0	0	10
b	1072	497	0	0	14
c	1072	562	99	95	12
d	1613	921	21	28	89
e	1613	593	511	512	88
f	270	85	4	4	6
g	270	80	786	800	7
h	2555	506	28	29	41

- a SRD reference fuel OP aged (64 hr at 95°C with 794 kPa oxygen)
b SRD + added indole OP aged
c SRD + added indole and phenalenone OP aged
d SRD + LCO extract OP aged
e SRD + LCO extract and added phenalenone OP aged
f SRD + LCO extract aged for 336 hr at 80°C
g SRD + LCO extract and added phenalenone aged for 336 hr at 80°C
h SRD + LCO extract aged for 65 hours at 120°C

Table 3. Variation of total alkylindole and phenalenone concentrations and total particulate on ageing SRD containing methanol extracts of LCO with and without added phenalenone.

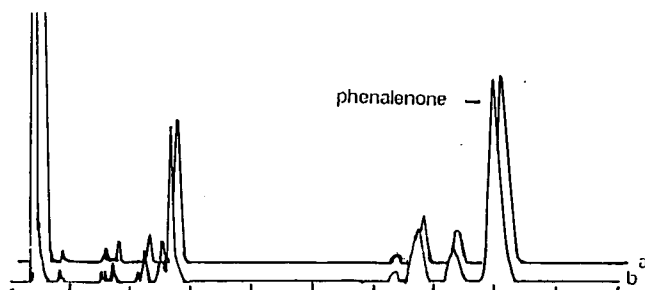


Figure 1. HPLC Chromatogram of absorption at 384 nm for SRD containing methanol extract of LCO, (a) before and (b) after ageing at 120°C for 65 hours.

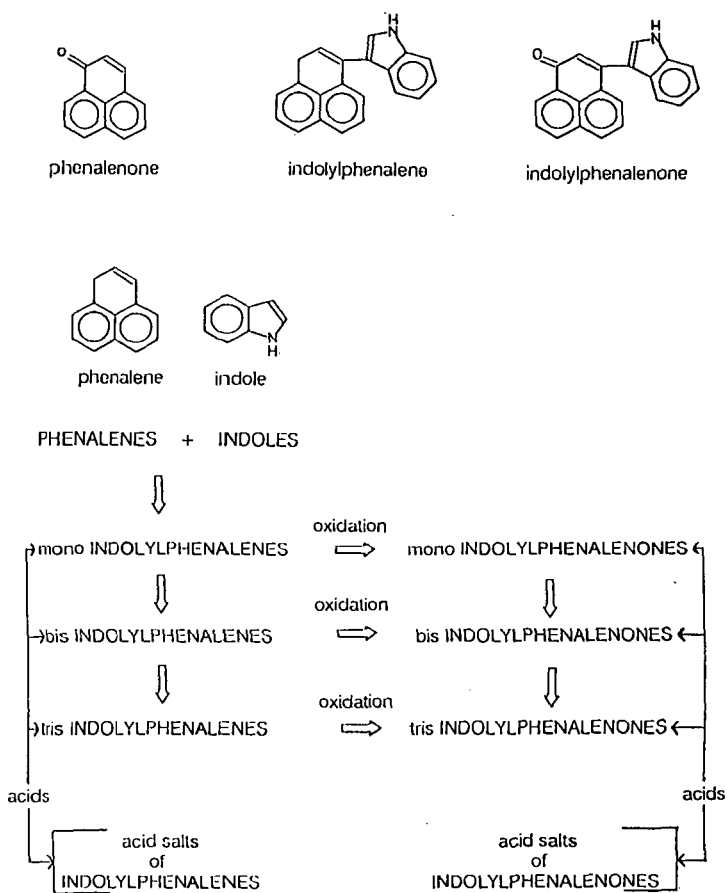


Figure 2. Possible Reaction schematic for formation of particulate from reaction of indole and phenalenone species.

SYMPOSIUM ON STABILITY AND OXIDATION OF MIDDLE-DISTILLATE FUELS
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AND
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COMBINED LIQUID CHROMATOGRAPHY/STABILITY TESTING (LC/ST) APPROACH
FOR ISOLATION OF COMPOUNDS RESPONSIBLE FOR FUEL INSTABILITY

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INTRODUCTION

The bulk of prior work on fuel stability problems indicates that the instability of a given fuel usually can be attributed to a relatively small subset of compounds/compound types which are typically present at low abundance in the fuel. For example, recent work has implicated alkylindoles, alkylphenalenes, and sulfonic acids as major contributors to storage instability of diesel fuel (1-12). Phenolic compounds also contribute to diesel sediment formation (13,14), and carboxylic or other acids of similar or greater acidity accelerate the rate of sediment formation (15).

Sediments formed during storage of jet fuels produced by hydrocracking processes largely contained aromatic hydrocarbons and oxygen-containing compounds (16). In the case of thermal instability of jet fuels, compounds that are either easily converted to peroxy radicals or hydroperoxides, or are important in propagation of the free radical reactions, are of greatest concern (10). Analysis of JFTOT tube deposits and those on filters downstream of the JFTOT tube has indicated contributions from a wider variety of compound types, relative to those formed in storage sediments (17,18).

A common feature of each type of stability problem cited above is the prominent role played by acidic compounds, either as catalysts or direct participants in sediment/deposit formation. Alkylindoles, sulfonic acids, phenolic compounds, carboxylic acids and hydroperoxides all exhibit acidic (hydrogen donor) properties. As a general correlation, Clark and Smith found that total acid content, as determined by yield of acids from nonaqueous ion exchange liquid chromatography, was the best available predictor of thermal stability (19).

Even where the components responsible for stability problems have been identified, there frequently are many unanswered questions concerning the nature of their interaction to form deposits/sediments, which compounds actually initiate or limit the sediment-forming process, and what reactions control the overall rate of sediment formation. Design of cost-effective methods or approaches to resolve a given stability problem normally requires at least some information concerning the sediment-forming process. For example, the effectiveness of tertiary amine additives in storage stabilization of diesel fuels containing light cycle oil may be attributed to their neutralization of acids which catalyze reactions resulting in gums and sediment (11,15).

Chemical separations have been shown to be an effective means for isolation of components that promote instability, as well as aiding in the determination of relevant reactions leading to deposit/sediment formation (e.g., 2,7,13,14). However, the availability of a general scheme for systematic separation of compound classes in jet or diesel fuels, plus a means for rapidly assessing the impact of the resulting fractions on stability, would further improve the applicability of this approach to fuel stability studies. This report describes a series of liquid chromatographic (LC) separations and reblending/stability testing techniques aimed at meeting this need. Representative results are provided to illustrate the merit of this approach as well as problems encountered in its use. In agreement with work cited above, acidic components are frequently implicated as primary promoters of instability from the results reported herein.

EXPERIMENTAL

Figure 1 outlines the complete sequence of available separations. Procedures for each separation step are described in detail elsewhere (20). Typically, stability testing (Figure 2) is performed after each stage of separation, and those results determine the extent and emphasis of additional separations. For example, further separations of neutrals into subtypes indicated in Figure 1 are not performed unless stability tests indicate significant deposit/sediment formation for the whole neutral fraction. Subfractionation of whole acids and bases is more commonly performed, since stability tests on acid + neutral or base + neutral blends frequently implicate one or both of those types as promoters/causes of instability. As noted in Figure 2, whole neutrals are typically used as the blend stock for acid/base fractions or subfractions. Fractions are usually reblended according to their proportions in the whole fuel. Comprehensive recomposites (e.g., acids + bases + neutrals) are tested at each stage of the work to check for bias in stability tests and/or contamination/losses during separations. Details of the storage (typically 2 weeks at 80° C) and thermal (modified D 3241) stability test procedures appear elsewhere (17,21,22).

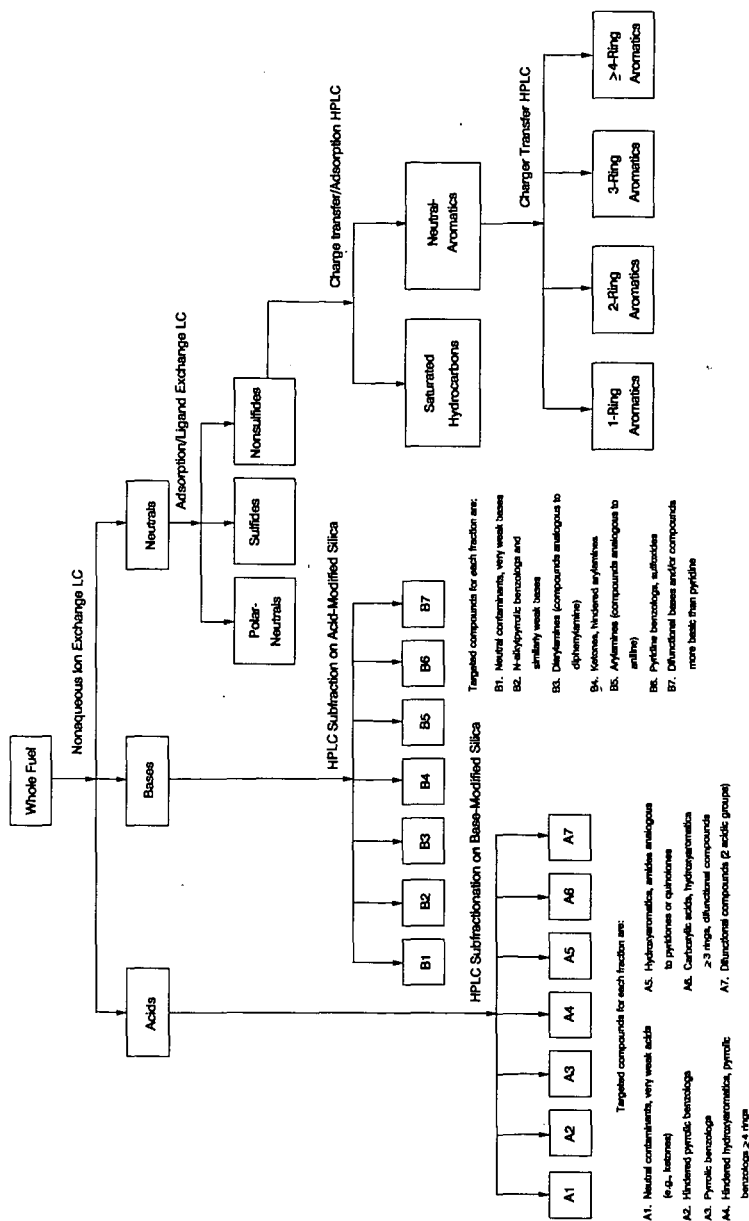


Figure 1. Schematic for LC Separations. Note that subfractionation of neutrals (i.e. into Polar-neutrals, sulfides, etc.) is not normally necessary, since neutrals are usually quite stable.

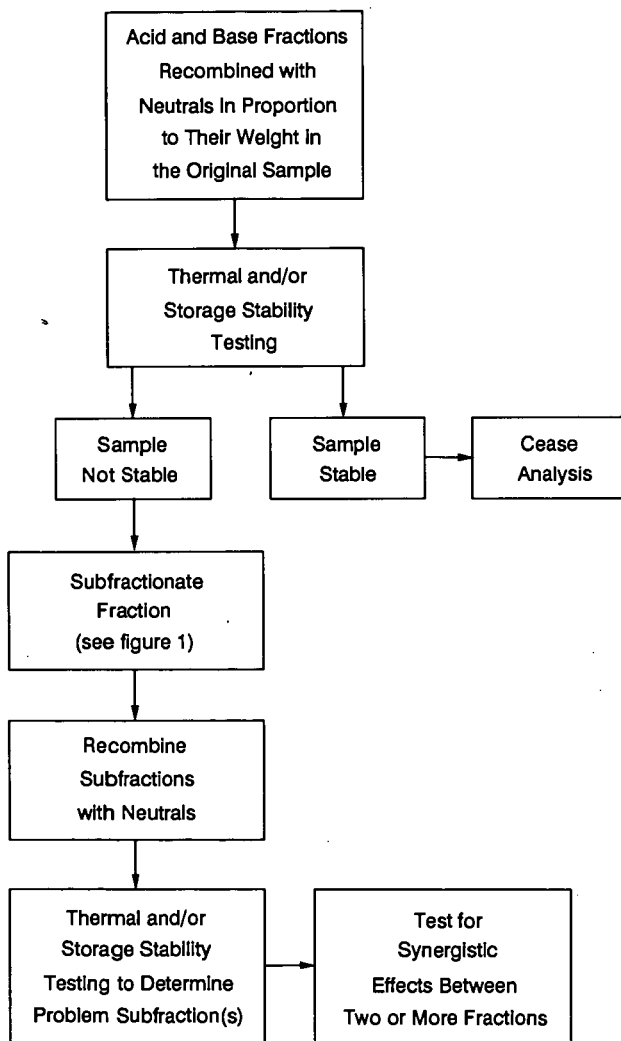


Figure 2. Typical Sequence for Reblending and Stability Testing of Acid and Base Fractions

RESULTS AND DISCUSSION

Tables 1 and 2 show comparisons of thermal stability of two jet fuels (NIPER sample Nos. 2140 and 2302) versus their neutral fractions under mild (Table 1) and moderate (Table 2) thermal stress conditions. The significantly greater thermal stability of neutrals relative to the whole fuel is quite evident from this data. Fraction yields (wt %) from separation of 2140 and 2302 fuels into acids, bases, and neutrals (ABN) were, respectively: 0.17(A), 0.08(B), 98.0(N) (98.2 total); 0.19(A), 0.04(B), 94.5(N) (94.6 total). Thus, removal of a relatively small proportion of acidic/basic material (ca. 0.25 wt %) greatly improved the thermal stability of these two fuels.

TABLE 1
Thermal Stability of Whole Jet Fuels vs. Neutral Fractions,
Standard JFTOT (2½ hrs. @ 260° C)

Sample No.	Fraction	Tube Rating	Pressure Drop (psi)
2140	Whole	4	0
2140	Neutral	1	0
2302	Whole	3	0
2302	Neutral	1	0

TABLE 2
Thermal Stability of Whole Jet Fuels vs. Neutral Fractions,
Extended JFTOT (277° C)

Sample No.	Fraction	Run Time	Tube Deposit Rating	Filter Pressure Drop (psi)
2140	Whole	12 hours	>>4 (black)	filter plugged
2140	Neutral	12 hours	2	0
2302	Whole	3.5 hours	>4 (brown)	filter plugged
2302	Neutral	3.5 hours	1	0

An earlier report discussed mass spectrometric (MS) analysis of JFTOT tube deposits and sediments from downstream filters from both the 2140 and 2302 fuels (17). Those results indicated a predominance of polar compounds in each case, especially when the MS sample introduction probe was heated above 150° C. Components vaporized at temperatures $\geq 150^\circ\text{C}$ were probably covalently bonded within the sediment structure (17). Thus, the observed improvement in thermal stability of neutrals versus whole fuels is consistent with the lower thermal stability of acidic and basic components indicated by MS analysis.

Because of the relatively large quantities of sample (ca. 500 mL) required by the JFTOT test, differential scanning calorimetry is currently being explored as an alternate means for evaluating the thermal stability of whole acid and base fractions and subfractions thereof. Those results will be reported in a later paper.

Tables 3 and 4 show separation and storage stability test results for a straight-run middle distillate (450-650° F, 0.5 wt % S, 34 °API). Although as a whole the results clearly show acidic types to be largely responsible for sediment formation in this case, close inspection of the data reveals some inconsistencies. The most significant discrepancy is the difference between total sediment for rebled acids + bases + neutrals versus the original distillate (22 versus 8.7 mg/100 mL). The main reason for the higher apparent sediment yield from the rebled sample was found to be incomplete dissolution of the acid fraction into neutrals during the rebleding step. The insoluble material in the acid fraction temporarily suspended into the neutrals (giving the appearance of dissolution), but ultimately added to the weight of insolubles obtained by filtration at the end of the stability test. This error is similarly reflected in the high apparent sediment yield for the acids + neutrals blend (21 mg/100 mL).

TABLE 3
Mass Balances from Separation of a North American
Straight-Run Middle Distillate

Fraction ¹	Yield (wt %)
Acids	0.47
A1	0.056
A2	0.019
A3	0.18
A4	0.036
A5	0.047
A6	0.063
A7	0.011
Total, A1-A7	0.412
Bases	0.17
B1	0.082
B2	0.001
B3	0.014
B4	0.013
B5	0.012
B6	0.036
B7	0.018
Total, B1-B7	0.176
Neutrals	98.1
Total, Acids + Bases + Neutrals	98.7

¹See Figure 1.

TABLE 4
Storage Stability Test Results on Fractions Listed in Table 3¹

Fraction	Total Sediment (mg/100 mL)	Net Sediment ² (mg/100 mL)
Acids	21	19
A1	2.7	0.5
A2	8.7	6.5
A3	2.1	-0.1
A4	2.2	0.0
A5	2.2	0.0
A6	7.0	4.8
A7	5.6	3.4
Total, A1-A7	-	15.1
Bases	2.9	0.7
B1	1.9	-0.3
B2	1.4	-0.8
B3	1.5	-0.7
B4	0.7	-1.5
B5	0.5	-1.7
B6	3.4	1.2
B7	5.9	3.7
Total, B1-B7	-	-0.1
Neutrals	2.2	-
Neutrals + Acids + Bases	22	20
Whole Distillate	8.7	-

¹80° C, 2 weeks, air at ambient pressure. Average of duplicate determinations is shown.

²Net sediment = total sediment - sediment from neutrals. (Neutrals were used as diluent for all acid and base fractions).

Because of the unreliability of simple visual inspection of reblended samples for assessment of solubility, they are now routinely prefiltered prior to stability testing. This precaution has significantly improved balances in stability test results for composited fractions versus whole materials over those obtained in early work such as that illustrated in Table 4. The source of the insoluble material is not well defined; contributions from solvent impurities and materials used in the separations (e.g., ion exchange resin artifacts) are suspected. In addition, degraded or otherwise altered fuel components probably make up part of the insoluble material in many cases. It should be emphasized that the overall magnitude of insolubles is quite small. For example, the acid fraction comprises 0.47 wt % (equivalent to ca. 425 mg/100 mL) of the middle distillate; the portion that did not dissolve (ca. 13 mg/100 mL) amounted to only about 3 percent of the acid fraction.

For the purpose of determining sediment directly attributable to a given acid or base fraction, the sediment formed by neutrals alone is typically subtracted from the total sediment for a given acid/base + neutrals blend (see "net sediment" data, Table 4). Although sediment formation may not be strictly an additive property, this or a similar practice is necessary to derive balances for sediment formation of individual fractions for comparison with the whole. Otherwise, the sediment contribution from the neutral fraction would be propagated in proportion to the number of fractions tested, and balances over fractions would invariably exceed that of the whole.

In light of the above discussion, it may be seen that most base sub-fractions from the middle distillate apparently stabilize the neutral fraction (B1-B5), and only two (B6 and B7) provide a positive net sediment yield. The balance for net sediment yield calculated over the base subfractions (-0.1 mg/100 mL) is within experimental error of that determined for the whole bases (0.7 mg/100 mL). In the case of the acid subfractions, the apparent sediment yield for A2 (6.5 mg/100 mL) is believed to have resulted largely from incomplete solution rather than actual sediment formation. Thus, the dominant sediment-forming acidic compounds are present in A6 and A7, which provide a combined sediment yield (8.2 mg/mL) consistent with that of the whole distillate (8.7 mg/mL). Thus, in the case of both acids and bases, compounds exhibiting the highest polarity/degree of functionality in terms of separation behavior (see the description of subfractions B6, B7, A6, and A7 composition in Figure 1) also show the highest sediment-forming tendency. Their combined concentration in the distillate is extremely low, ca. 0.1 wt %. Effective removal or neutralization of the effects of these compounds should improve the storage stability of the distillate to the level of sediment formation exhibited by the neutral fraction (2.2 mg/100 mL).

CONCLUSIONS

The combination of LC separation and stability testing (LC/ST) is an effective screening tool for identifying components/compound types that promote instability. The LC fractions also constitute a valuable resource for studying sediment formation pathways, synergistic effects between different compound types, and the effectiveness of potential stabilizing additives.

The sensitivity of stability tests to contamination and sample alteration occurring during LC separations places stringent demands on the LC methodology, solvents and materials used, and procedures employed during work-up of fractions and their storage prior to testing. However, the simplicity and direct relevance of stability test results to the issue of fuel stability makes it the method of choice for evaluation of fractions. In contrast, detailed analysis of fresh versus aged fuel fractions proved to be a very laborious approach for estimating their stability (23). Thus, the prudent course of action is to improve separation and reblending techniques where necessary, rather than to look for alternate methods for fraction evaluation.

Although more difficult experimentally, work with actual fuel fractions provides a more realistic assessment of stability problems than possible with simple model systems.

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STORAGE STABILITY OF FUELS - IDENTIFICATION OF NITROGEN COMPOUNDS AND THEIR EVOLUTION DURING AGEING IN ABSENCE AND PRESENCE OF ADDITIVES by M. Dorbon, C. Bernasconi*, J. Gaillard, J. Denis, Institut Francais du Petrole, FRANCE and *ELF FRANCE, Centre de Recherche de Solaize, FRANCE

INTRODUCTION

The growing need for Diesel fuels and developments in refining processes, particularly the increased use of Fluid Catalytic Cracking (FCC), have led refiners to consider introducing Light Cycle Oils (LCOs) in formulations of distillates for home-heating oils and Diesel fuels.

Unfortunately, the cracking products often undergo changes, and induce darkening and the formation of insolubles liable to cause difficulties in use.

The degradation mechanisms have not yet been clearly identified despite many interesting investigations already conducted. Taylor and Frankenfeld¹ reviewed a number of hypotheses and conclusions drawn from previous studies, and stressed the determining role of oxidation. Many articles have suggested that carboxylic, phenolic and sulfonic acids produced by the oxidation of middle distillates exert a catalytic effect on fuel instability^{2, 3, 4} and on the quantity of sediments formed⁴. Bhan *et al*⁵ demonstrated that aromatic compounds and non-basic nitrogen compounds, could be the main source of sediment formation. Recently, Pedley *et al*^{6, 7} found that a major source of strongly-colored sediments was the oxidation of phenalene to phenalenone, followed by the reaction of phenalenone with alkyl indoles, yielding addition products that precipitate under the influence of sulfonic acids, themselves produced by the oxidation of thiols.

In previous work⁸ we found that most of the changing compounds were located in the heaviest distillation fraction of LCO (BP > 310 to 315 °C) and that better stability could be achieved by removing this fraction.

Among these compounds, those containing nitrogen were largely identified⁹, showing that LCOs always contain three clearly distinct main groups of nitrogen compounds: anilines, alkyl indoles and alkyl carbazoles, and that only the alkyl indoles are subject to change during degradation in storage.

This identification led to the development of a method for determining the changes in alkyl indoles during the storage of several mixtures of straight-run distillates and LCOs in the absence and presence of additives.

EXPERIMENTAL

Several middle distillates were employed and several additives were tested for this investigation.

Middle distillates

- | | |
|---------------------------------------|---------------|
| •Three straight-run distillates (SR): | B1 and C1, E1 |
| •Three low-sulfur LCOs: | B2 and C2, D2 |
| •Three high-sulfur LCOs: | B3 and C3, D3 |

The properties of these materials are listed in Table 1. All the ageing tests were performed on LCOs and mixtures in 70/30 proportions of SR distillate and LCO. The sulfur content for some of them was accordingly higher than the present French specification of 0.3% S, but this makes the alteration effect of LCOs more pronounced.

Additives

- AD1 and AD2, mixtures of tertiary amines and metal deactivator.
- AD3, multi-purpose additive containing tertiary amines, metal deactivator and dispersant.

These additives were used mainly at 40 and 200 ppm by weight.

Ageing test methods

Three ageing test methods were employed in the laboratory.

- A highly-accelerated method, in which 350 ml of mixture is subjected for 2 h at 120 °C to a stream of 3 l/h of pure oxygen. The apparatus and bottles used are similar to those of method ASTM D-2274. The insolubles are determined by filtration through a 0.8 µm porosity cellulose acetate filter (Millipore filter AA).

The amounts of insolubles adhering to the tube walls after only 2 h were too small to be recovered.

- A similar method to ASTM D-4625, in which 300 ml of mixture is placed in contact with atmospheric air in glass bottles at 43 °C for 12 weeks. The filtrable and adhering insolubles are determined as in ASTM D-4625, except that 0.8 µm cellulose acetate filters are used instead of 1.5 µm glass fibers filters.
- A method corresponding to conditions approaching reality, in glass bottles for one year at room temperature in air. Filtrable and adhering insolubles are determined as above.

For these three methods, the color determinations of new and aged samples were performed according to ASTM D-1500.

These three methods can be considered as complementary owing to the different operating temperatures and atmospheres.

Method for analyzing nitrogen compounds

The selective detection of nitrogen compounds by gas-phase chromatography was performed using a Perkin Elmer 8500 chromatograph equipped with a thermo-ionic detector (NPD) and a packed column injector, modified for megabore capillary columns. The column was a 15 m x 530 µm i.d. fused silica capillary column, coated with a non-polar methyl silicon phase. The temperatures were programmed as follows: from 60 to 160 °C at 2.5 °C·min⁻¹, and from 160 to 200 °C at 2 °C·min⁻¹.

RESULTS AND DISCUSSION

Ageing of middle distillates in the absence of additives

Several straight-run middle distillates and low- and high-sulfur LCOs and mixtures of SR distillates and LCOs (70/30) were subjected to the three ageing tests in the laboratory. Table 2 shows the results in colors and weights of insolubles obtained by these tests.

- It appears that the straight-run middle distillates as such are stable, except in color, irrespective of the operating conditions, temperature and duration.
- Pure LCOs, however, are very unstable over long periods at low temperature, particularly high-sulfur LCOs. Most of the insolubles are found in the form of sediments adhering to the bottle walls.

In short-term tests at high temperature, stability appears to be satisfactory.

- Mixtures of straight-run distillates and LCOs display stability that depends on both of the components. Mixtures based on B1 display greater changes than those based on C1. For B1, the weights of insolubles are higher than anticipated from the results obtained on the two pure components. Filtrable insolubles are present in larger quantities than adhering insolubles. These two remarks do not apply to mixtures based on SR distillate C1. As to the influence of LCOs, as anticipated, mixtures containing low-sulfur LCOs are more stable than those containing high-sulfur LCOs.

If the methods are compared, it appears that the twelve-week method at 43 °C in air is very closely correlated with storage at room temperature. The two-hour method at 120°C in oxygen appears less severe.

Ageing of middle distillates in the presence of additives

Three types of additive, in concentrations of 40 and 200 ppm, were added to the SR distillates/LCOs mixtures B1/B3, C1/C2 and C1/C3, and aged by the three laboratory methods. Table 3 shows the results in color and weight of filtrable and adhering sediments. As a rule, the additives are ineffective against a color change. From the standpoint of sediments, the first two additives AD1 and AD2, based on aliphatic or cyclo-aliphatic tertiary amines combined with a metal deactivator, appear to be more effective according to the accelerated method at 120 °C than with the long-term storage methods at low temperature. The increase in concentration from 40 to 200 ppm does not improve a lot effectiveness according to these tests. Additive AD3, which also contains a dispersant, is more effective in the long-term test, and the concentration effect is significant.

The distribution of the sediments also differs in the long-term tests. With AD1 and AD2, adhering insolubles are higher than filtrable insolubles, and vice versa with AD3. The dispersant component of AD3 tends to keep the insolubles in suspension.

Analysis of ageing as a function of time

To gain a better understanding of the mechanisms of sediment formation and additive action in middle distillates during the different accelerated and long term ageing methods, a kinetic analysis was performed on several SR distillates, LCOs and SR/LCO mixtures (70/30) in the absence and presence of additives.

• Test at 120°C

For this kinetic analysis, two mixtures B1/B2 (70/30) and B1/B3 (70/30) alone and with 40 ppm of AD1 additive were subjected to ageing testing in oxygen for times ranging up to 40 hours (figure 1). A large amount of insolubles is formed during the first few hours, and the increase is then slower. The effectiveness of additive AD1 is substantial, especially during the first hours of rapid change, and then declines but still remains high :

• Tests at 43°C in the absence of additives

Figure 2 shows the curves obtained for constituents and mixtures in 12 weeks tests at 43°C. These curves have various configurations :

- SR distillates C1 and E1 have almost linear increases in insolubles content.
- LCOs give curves with varying configurations. For C2 and C3, a short induction period appears, followed by an abrupt increase in insolubles weight; whereas for D2 and D3, the increase is gradual and stabilization occurs after 8 weeks . Note the difference in scale between low sulfur LCOs and high sulfur LCOs.
- SR distillate / LCO mixtures have highly varying curve configurations as well.

• Tests at 43°C in the presence of additives

Figure 3 shows the curves obtained for SR distillate/LCO mixtures (70/30) in the absence and presence of additives. Additives diminish the amounts of insolubles formed without changing the general configuration of the curves, but preventing the formation of insolubles from reaching too high values.

Changes in nitrogen compounds: analytical method

An analytical procedure was previously developed to identify the nitrogen compounds in LCOs⁹. The same nitrogen compounds were found in many LCOs: aniline and alkyl anilines from C1 to C4, indole and alkyl indoles from C1 to C4, carbazole and alkyl carbazoles from C1 to C3 (Figure 4). Very few differences were observed in the relative proportions of each compound.

The principle of the method is the selective extraction of the nitrogen compounds by liquid chromatography and the analysis of the nitrogen extracts by coupling gas-phase chromatography with mass spectrometry (GC/MS), and by gas-phase chromatography with a specific thermo-ionic detector of nitrogen compounds⁹.

Due to the similarity of composition of the LCOs, it is unnecessary to extract the nitrogen compounds from each sample analyzed. To monitor the changes, these clearly identified compounds are analyzed by gas-phase chromatography with nitrogen specific thermo-ionic detector.

This analytical method can only be qualitative for the following reasons.

- (a) The response of each compound to the detector depends chiefly on the number of nitrogen atoms in the molecule, and also on the type of compound. Owing to the absence of pure compounds, it is impossible to determine the response factor of each compound.
- (b) The proportion of each of these compounds is close to the detection limit, leading to difficulties of integration.

However, the method serves to compare the relative amounts of each nitrogen compound, either between different samples, or between the same samples before and after ageing.

It was previously demonstrated that most of the alkyl indole peaks drop sharply during ageing, whereas the alkyl carbazoles are relatively unaffected (Figure 5). Carbazole in particular was found in the LCOs one of the most important and one of the least altered compounds during storage. This was confirmed by an outside calibration: the height of the carbazole peak remains constant within the experimental errors, for new and aged samples. Hence it proved convenient to use the carbazole in the LCOs as an internal standard. To compare the changes in the alkyl indoles, the ratios of the carbazole/alkyl indole peak heights were determined in different ageing tests, for example as a function of storage time.

Among the 24 alkyl indole peaks counted from 15 to 38 in Figure 4, the eight highest were selected to monitor the changes in these carbazole/alkyl indole peak height ratios. These peaks were:

- 15 and 17 methyl indoles or C1 indoles,
- 19 and 21 C2 indoles,
- 26, 27, 28, 29 C3 indoles.

To assess the significance of this method, a number of repeatability tests were performed on three new and aged C1/C3 samples by successive injections or at intervals of a few days.

Table 4 gives the results of this study.

Changes in the nitrogen compounds observed by gas-phase chromatography analyses were monitored in the following two studies:

- degradation kinetics in ageing tests for LCOs, and for straight-run distillate/LCO mixtures,
- the influence of multi-purpose additives on the ageing degradation of mixtures of straight-run distillates and LCOs.

Effect of test duration on changes in nitrogen compounds

The following products were subjected to ageing:

- LCOs: low-sulfur B2 and high-sulfur C3,
- SR distillate B1/LCO B2 mixture (70/30), and SR distillate B1/LCO C3 mixture (70/30).

The following ageings were carried out:

- at 120 °C in oxygen up to 8 h,
- at 43 °C in air up to 12 weeks.

The results in carbazole/alkyl indole ratios as a function of time are given in Figures 6a, 6b, 6c and 6d for the four products aged at 120 °C. An increase in this ratio can be observed, namely a progressive decrease in the alkyl indole peaks, particularly the C1 and C2 indoles and two of the C3 indoles (26 and 28). This tendency is similar for the four products. As an example, Figure 5 shows a comparison between the NPD chromatograms of LCO B2 before and after ageings. The indole itself (peak 11) also decreases very substantially, but the height of this peak is very difficult to measure in most of the chromatograms, and the corresponding values could not be plotted on the diagrams.

At 43 °C in air, for the same four products, the changes in the nitrogen compounds shown in Figures 7a, 7b, 7c and 7d are similar to those observed at high temperature.

It is interesting to observe that a comparison of these results relative to the decrease in alkyl indoles shows that substantially equivalent values in weights of insolubles are obtained in three months at 43 °C and in 5 to 10 h at 120 °C. This confirms the relationship that may exist between the reactivity of the alkyl indoles and the storage instability of LCOs alone and in mixtures.

Effect of multi-purpose additives on the reactivity of alkyl indoles

Multi-purpose additives AD1, AD2 and AD3 were added at the rate of 40 and/or 200 ppm to the three distillate/LCO mixtures:

- SR distillate B1/ high-sulfur LCO B3 (70/30),
- SR distillate C1/ high-sulfur LCO C3 (70/30),
- SR distillate C1/ low-sulfur LCO C2 (70/30).

These mixtures were subjected to the following ageing tests :

- at 120 °C in oxygen for 2 h,
- at room temperature in air for 12 months.

In addition to the gravimetric determinations performed after filtration of the insolubles (Table 3), the nitrogen compounds were analyzed to monitor their changes.

For the comparative tests performed at 43 °C in 12 weeks, the weights of insolubles are shown in Table 3, but the nitrogen compounds were not analyzed.

Effect on B1/B3 mixtures:

The results are shown in Figures 8a and 8b in the form of the same diagrams as for the previous study, in ratios of carbazole/alkyl indole peak heights for the eight highest peaks.

In the absence of additive, the variation in these ratios or the decrease in alkyl indoles are more pronounced at 120 °C than at room temperature, whereas the weights of insolubles are higher at room temperature than at 120 °C.

Additives AD1, AD2 and AD3 are effective in preventing the reaction of alkyl indoles, because, for all the peaks, they return the carbazole/alkyl indole ratios to values close to the initial values before ageing. This is especially valid for AD1 at 120 °C and at room temperature, and for AD3 at room temperature, whereas the weights of insolubles remain relatively high despite the presence of these additives at room temperature particularly.

Effect on C1/C3 mixtures:

Similar results are shown in Figures 9a and 9b for these mixtures.

The diagrams have the same pattern as the foregoing: increase in the peak ratios, hence decrease in alkyl indoles when ageing without additive, but maintenance of peak ratios at intermediate values or close to the initial values for ageings in the presence of additives. Additive AD1 is more effective for the test at 120 °C than for the test at room temperature, while additive AD3 is highly effective in both types of test. At 40 ppm, and, above all, at 200 ppm, the alkyl indole peaks practically return to their initial value.

For all these C1/C3 mixtures, the weights of insolubles are too low at 120 °C to compare the effect of the additives from this standpoint. At room temperature, however, the weights of insolubles still remain high in the presence of additives, as for the B1/B3 mixtures.

Effect on C1/C2 mixtures:

For C1/C2 mixtures, the weights of insolubles are very low, and demonstrate the good storage stability of these products in mixtures. Tests with additives were not performed at 120 °C. The chromatographic analyses show in Figure 10 that the alkyl indoles preserve their initial content in the ageing test in the absence or presence of additives, which agrees with the relationship between the reactivity of the alkyl indoles and the storage stability.

The investigation of the influence of storage time on the behavior of LCOs and distillates containing a certain proportion of LCO revealed a close correlation between the formation of insolubles and the progressive disappearance of alkyl indoles, providing confirmation of the degradation mechanism proposed by Pedley *et al* 6.

According to this mechanism, moreover, the alkyl indoles only react in the presence of other oxidizable compounds. The products that react with alkyl indoles are perhaps absent in this case. This could explain the fact that in C1/C2 the alkyl indoles are present and not reactive.

The influence of additives on this variation in alkyl indole content during ageing is highly significant. On the one hand, they display great effectiveness in preventing the progressive disappearance of alkyl indoles, because chromatography shows that the alkyl indole peaks retain their initial value. On the other, they are less effective in preventing the formation of insolubles. Hence it appears that other products and other mechanisms are also involved in the degradation of LCOs, independent of the alkyl indoles, and that the additives are poorly effective in combating the detrimental effect of these other products.

CONCLUSIONS

This research project follows an analytical study concerning the identification of nitrogen compounds in middle distillates from fluid catalytic cracking (LCOs) ⁹.

The development of a method for monitoring the changes in nitrogen compounds served to observe the progressive decrease in the indole and alkyl indole contents during actual and laboratory storage tests on LCOs and mixtures of uncracked distillates and LCOs.

A comparison between the weights of insolubles determined during storage and the decrease in alkyl indoles confirms the degradation mechanism proposed by Pedley *et al* ⁶, namely the oxidation of phenalene to phenalenone, followed by the reaction of phenalenone with alkyl indoles, yielding precipitates under the influence of sulfonic acids resulting from the oxidation of thiols.

The analyses performed after the ageing tests conducted in the presence of additives showed that the alkyl indoles retain their initial value, while insolubles are still being formed. This would tend to show that some insolubles could be formed by mechanisms different from the one involving alkyl indoles.

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TABLE 1

CHARACTERISTICS OF MIDDLE DISTILLATES

Characteristics		SR distillates			Low-sulfur LCOs			High-sulfur LCOs		
		B1	C1	E1	B2	C2	D2	B3	C3	D3
Flash point	°C	111	106	102	85	92	71	81	70	72
Cloud point	°C	7	-8	-1	-10	-9	-37	-10	-15	-10
Cold filter plugging point	°C	6	-9	0	-15	-11	-37	-23	-17	-19
Pour point	°C	3	-12	-3	-27	-21	<-42	-43	-24	-36
Sulfur	%	0.14	0.04	0.11	0.84	0.51	0.59	2.54	1.31	1.69
Total nitrogen	ppm	265	10	230	630	670	510	440	590	685
Basic nitrogen	ppm	170	7	58	100	75	106	90	99	115
Viscosity at 20°C	mm ² /s	9.4	5.41	6.53	3.79	4.56	2.94	3.53	3.59	3.89
Density at 15°C	kg/l	0.8639	0.8276	0.8438	0.9355	0.9106	0.8996	0.9382	0.9118	0.9262
DISTILLATION										
Initial boiling point	°C	232	220	200	148	191	150	120	132	138
Final boiling point	°C	402	355	358	339	354	311	334	342	344
MASS SPECTROMETRY										
Paraffins	%	27.4	41.8		14	12.2		10.8	11.7	
Naphthenes	%	43.2	40.5		9.2	16.8		7.8	9.8	
Monoaromatics	%	7	3.7		10.9	10.6		11	12.1	
Diaromatics	%	13.9	8.2		38.3	34.3		38.1	37.7	
Triaromatics	%	6.6	4.4		18	17.5		13.4	14.7	
Benzothiophenes	%	1.5	0.6		6.7	5.7		15.8	10.7	
Dibenzothiophenes	%	0.4	0.8		2.9	2.9		3.1	3.3	

TABLE 2

STABILITY TESTS OF DISTILLATES PURE AND IN MIXTURES

Distillates	Initial color (ASTM D1500)	Insolubles before test mg/100 ml	After 2h. 120°C in O ₂		After 12 weeks. 43 °C in air				After 1 year at room temperature in air			
			Color	total Insolub.*	Color	Filterable insolub.	Adhering insolub.	Total insolub.	Color	Filterable insolub.	Adhering insolub.	Total insolub.
SR middle distillates												
B1	1	0.2	1.5	0.4	3.5	0.5	0	0.5	2.5	0.3	0.5	0.8
C1	0	nd	0	0.1	0.5	0	0.3	0.3	0.5	0.1	1.5	1.6
Low-sulfur LCOs												
B2	2.5	nd	3.5	0.5	H8	2.5	20.9	23.4				
C2	1.5	nd	2.5	0.1	7	6.4	10	16.4	6	6.9	4.7	11.6
High-sulfur LCOs												
B3	2	0.2	<3.5	0.2	7.5	0.8	37.1	37.9				
C3	1.5	nd	3	0.2	7.5	34.7	10.7	45.4	7.5	42.3	17.1	59.4
70/30 mixtures												
B1/B2	2	0.1	6	1.6	6	7.9	4.1	12				
B1/C2	2	nd	<3.5	0.7	5.5	6.5	2.8	9.3				
C1/C2	1	0.1	1.5	0.1	2.5	0.4	1.4	1.8	2.5	0.2	1.7	1.9
B1/B3	2	0.1	6.5	13.8	5.5	11.6	5.4	17	5.5	12.6	4.7	17.3
B1/C3	2	0.2	5	5	5.5	3.8	5.9	9.7				
C1/C3	1	0.1	1.5	0.3	2.5	0.4	6.6	7	3	5.8	3.7	9.5

* No adhering insoluble by this method

TABLE 3

**STABILITY TESTS OF MIDDLE DISTILLATES IN MIXTURES
WITH ADDITIVES**

Distillates + additives	Initial color (ASTM D1500)	Insolubles before test mg/100 ml	After 2h. 120°C in O ₂		After 12 weeks. 43 °C in air				After 1 year at room temperature in air			
			Color	total insolub.*	Color	Filterable insolub.	Adhering insolub.	Total insolub.	Color	Filterable insolub.	Adhering insolub.	Total insolub.
B1/B3 (70/30)	2	0.1	6.5	13.8	5.5	11.6	5.4	17	5.5	12.6	4.7	17.3
+ AD1 40 ppm	"	"	5	3.1	5.5	3.8	4.2	8	5.5	6.6	4.1	10.7
+ AD1 200 ppm	"	"	nd	nd	5.5	1.6	5.4	7	5.5	5.3	5.9	11.2
+ AD2 40 ppm	"	"	6	3.1	5.5	2.9	6.3	9.2				
+ AD3 40 ppm	"	"		nd	7	3.8	0.7	4.5				
+ AD3 200 ppm	"	"			7	3.8	0.7	4.5	6.5	5.1	2.5	7.6
C1/C2 (70/30)	1	0.1	1.5	0.1	2.5	0.4	1.4	1.8	2.5	0.2	1.7	1.9
+ AD1 40 ppm	"	"		nd	3	0.6	1.8	2.4	3	0.3	2.7	3
+ AD1 200 ppm	"	"							3	0.5	2.1	2.6
+ AD3 40 ppm	"	"		nd	3	0.8	0.6	1.4	3	0.8	0.4	1.2
+AD3 200 ppm	"	"							3	0.2	1	1.2
C1/C3 (70/30)	1	0.1	1.5	0.3	2.5	0.4	6.6	7	3	5.8	3.7	9.5
+ AD1 40 ppm	"	"	1.5	0.1	2.5	1.3	4.2	5.5	3	0.8	7.8	8.6
+ AD2 40 ppm	"	"	1.5	0.1	3	3	4.9	7.9				
+ AD3 40 ppm	"	"	1.5	0.2	2.5	4.9	0.8	5.7	3	4.8	2.4	7.2
+ AD3 200 ppm	"	"	1.5	0.2					3	2.6	1.6	4.2

*No adhering insoluble by this method

TABLE 4

REPEATABILITY OF DETERMINATIONS OF
CARBAZOLE/ALKYL INDOLE PEAK HEIGHT RATIOS
BY GAS-PHASE CHROMATOGRAPHY

Sample	Date	Peak 15	Peak 17	Peak 19	Peak 21	Peak 26	Peak 27	Peak 28	Peak 29
C1/C3 no aged	4/14/89	0.9	0.5	0.33	0.33	0.8	0.9	0.75	0.7
	4/17/89	1.1	0.55	0.31	0.34	0.7	0.9	0.9	0.7
C1/C3 aged at 120°C	4/14/89	1.3	0.7	0.55	0.53	1	0.96	1	0.85
	4/17/89	1.4	0.8	0.6	0.53	0.9	0.92	1.05	0.9
C1/C3 aged with AD2 at 120°C	4/14/89	1.3	0.55	0.4	0.4	0.8	1.1	1.1	0.8
	4/18/89	0.95	0.55	0.35	0.35	0.75	0.9	0.8	0.7
	4/18/89	0.95	0.5	0.3	0.35	0.7	0.85	0.75	0.7

FIGURE 1
AGEING KINETICS AT 120°C IN OXYGEN

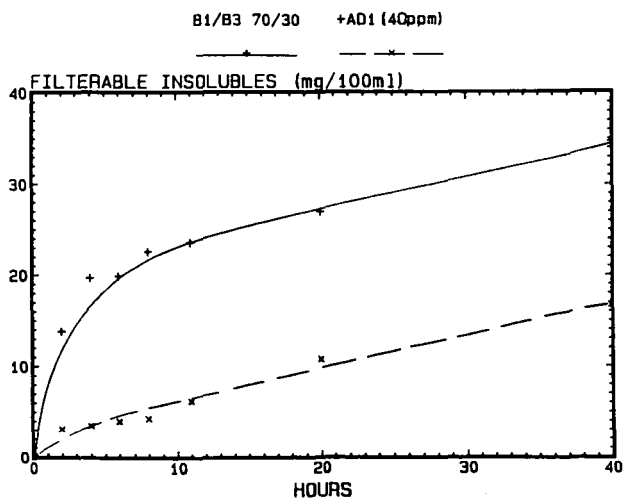
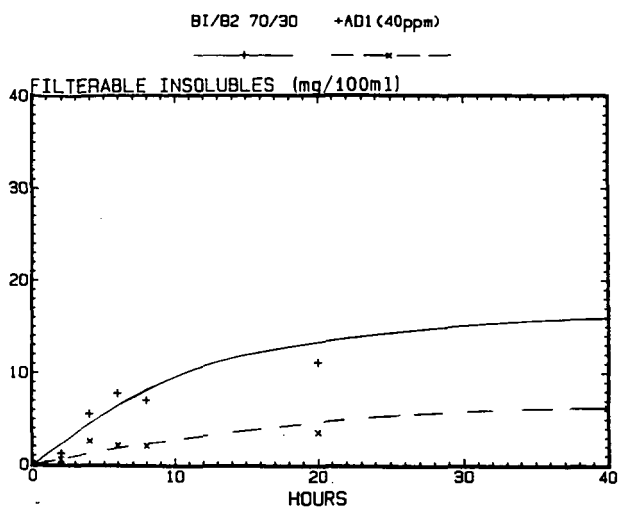


FIGURE 2
AGEING KINETICS AT 43°C IN AIR (WITHOUT ADDITIVES)

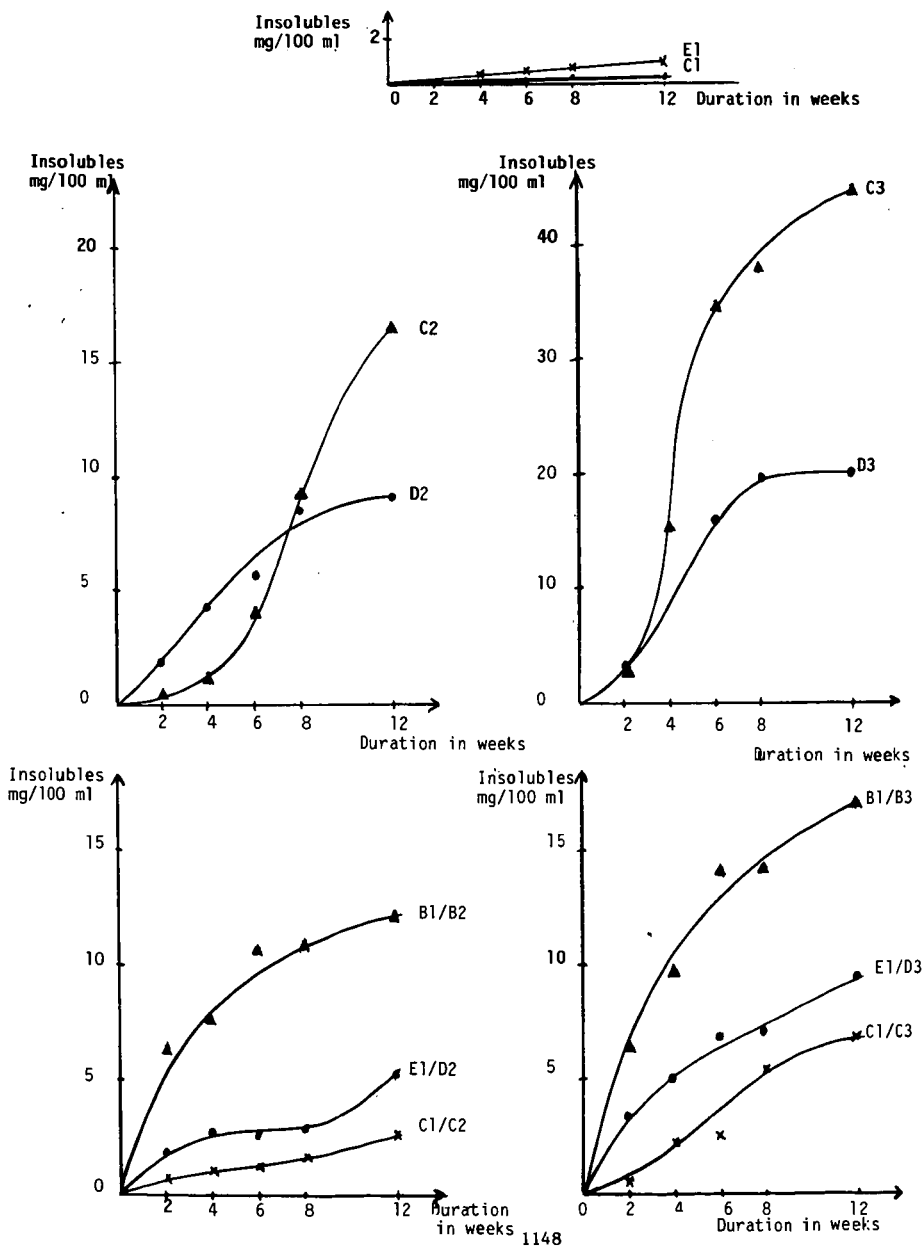


FIGURE 3

AGEING KINETICS AT 43°C IN AIR (WITH ADDITIVES)

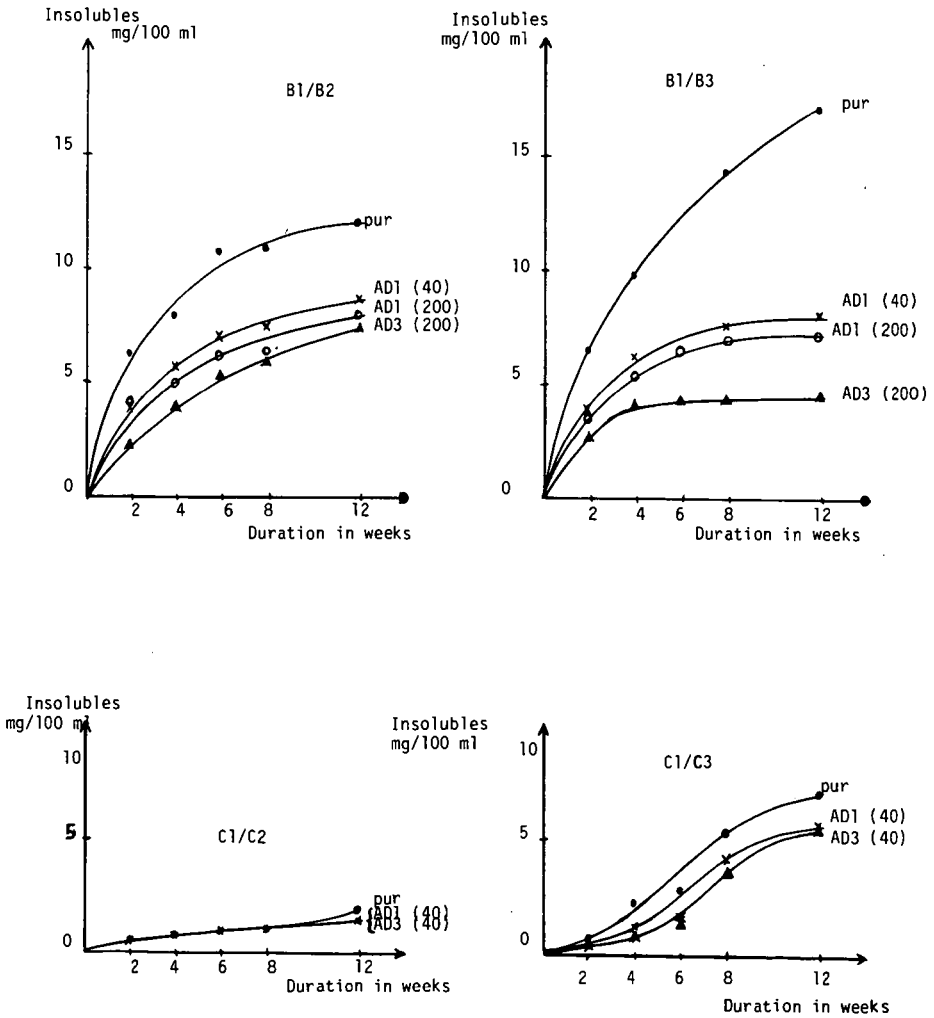


FIGURE 4
NPD CHROMATOGRAM OF NITROGEN COMPOUNDS IDENTIFIED IN A LCO

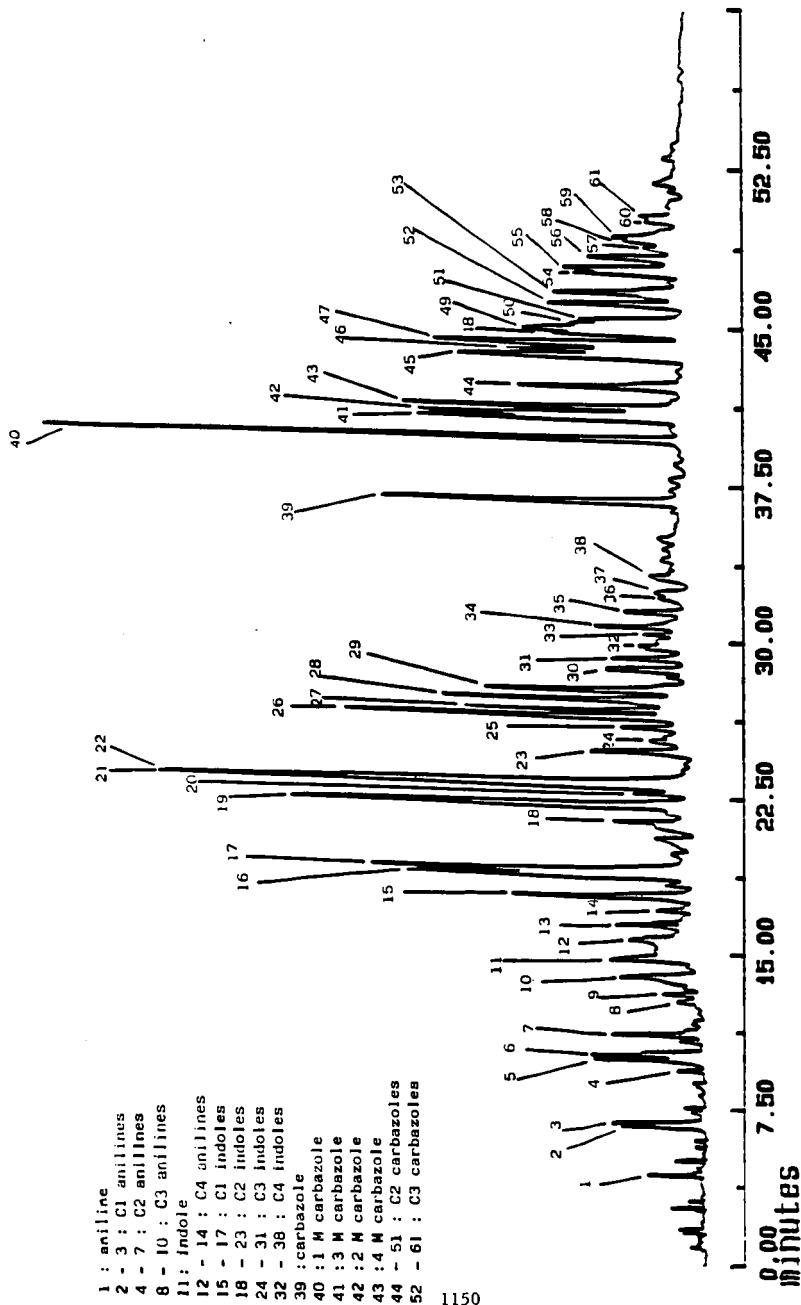
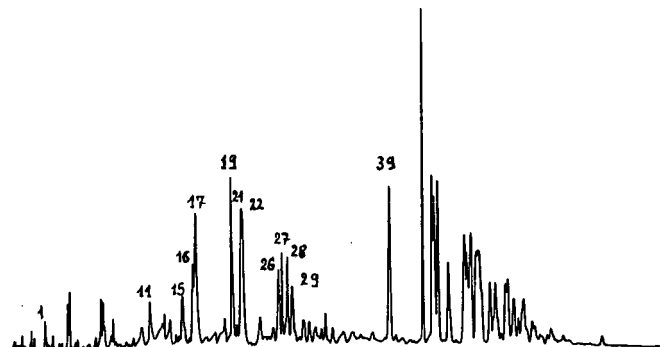
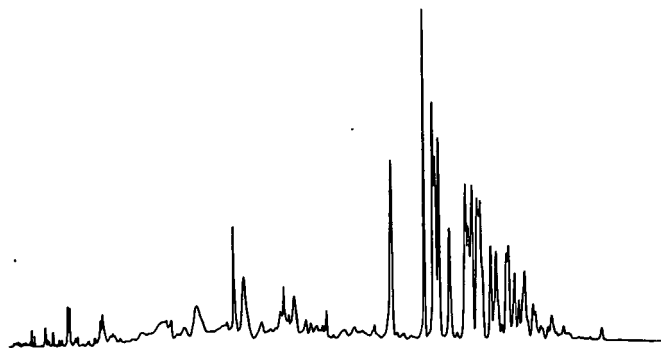


FIGURE 5
 NPD CHROMATOGRAMS OF LCO B2, BEFORE AGEING, AFTER AGEING AT 43°C,
 AND AFTER AGEING AT 120°C

LCO B2



LCO B2
 12 WEEKS AT 43°C



LCO B2
 8 HOURS AT 120°C

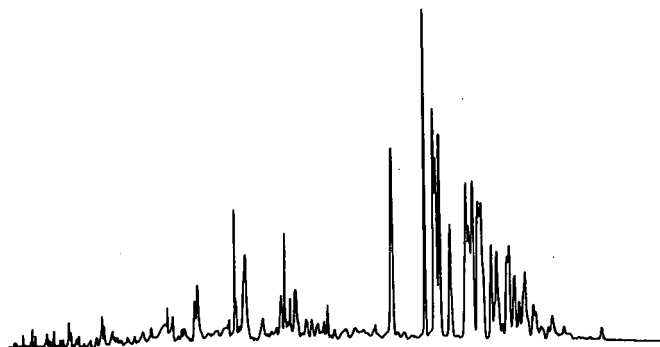


FIGURE 6
NITROGEN COMPOUNDS AS A FUNCTION OF TIME AT 120°C

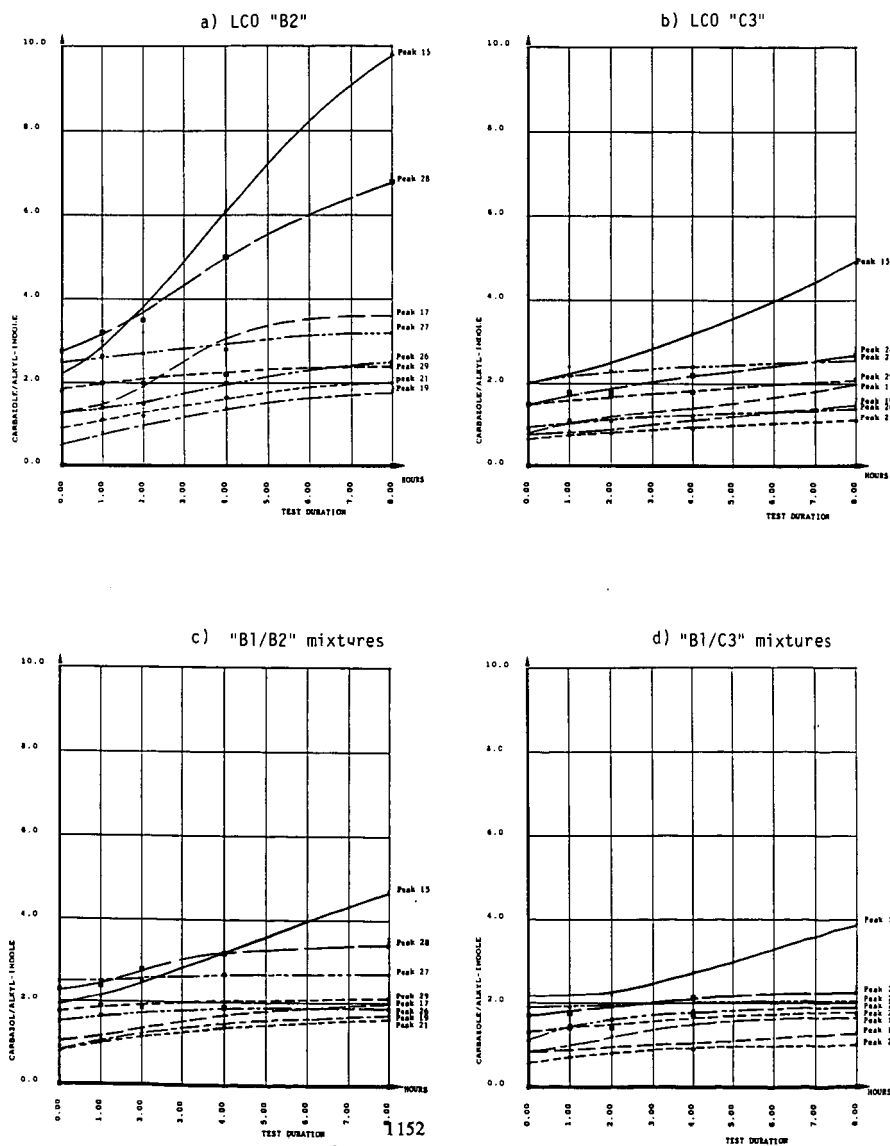


FIGURE 7
NITROGEN COMPOUNDS AS A FUNCTION OF TIME AT 43°C

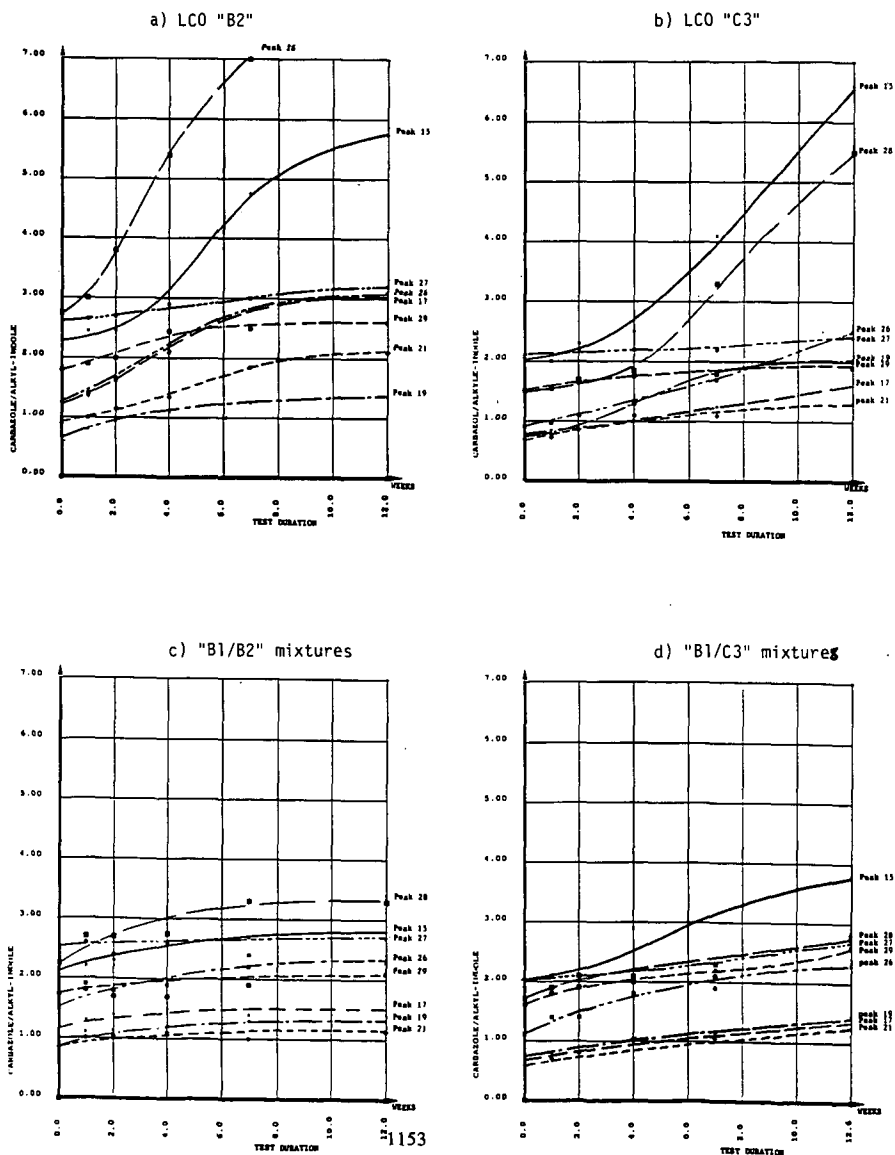


FIGURE 8
INFLUENCE OF ADDITIVES ON CHANGES IN NITROGEN COMPOUNDS IN B1/B3 70/30 MIXTURES
SUBJECTED TO AGEINGS

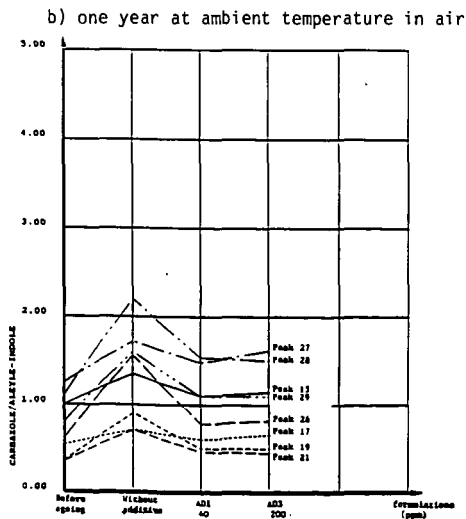
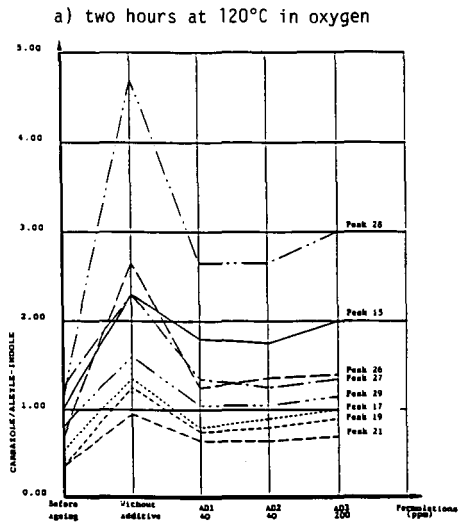


FIGURE 9

INFLUENCE OF ADDITIVES ON CHANGES IN NITROGEN COMPOUNDS IN C1/C3 70/30 MIXTURES
SUBJECTED TO AGEINGS

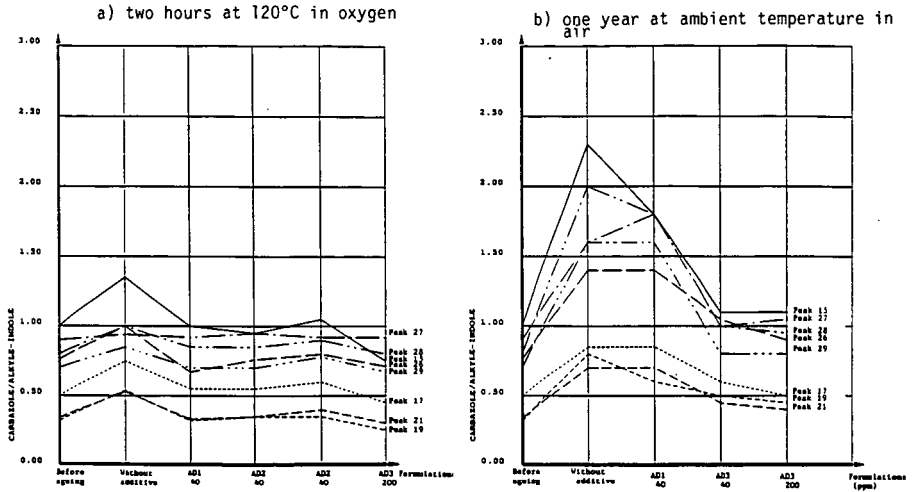
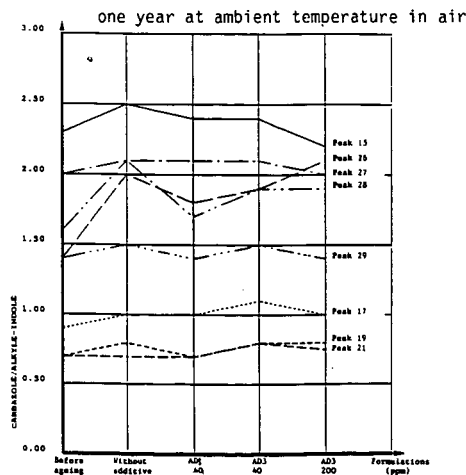


FIGURE 10

INFLUENCE OF ADDITIVES ON CHANGES IN NITROGEN COMPOUNDS IN C1/C2 70/30 MIXTURES
SUBJECTED TO AGEINGS



CHEMICAL EXAMINATION OF DISTILLATE FUEL DEPOSITS FORMED DURING STORAGE

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INTRODUCTION

Storage stability of distillate fuels has been of modest concern for fuels made by refining processes based on straight run distillation. However, increasing quantities of heavy crudes are being run in refineries using catalytic cracking processes to increase the yield of middle distillate fuels. The cracked products, which contain chemically unstable species, are blended into straight run streams. The unstable components, although diluted by the blending, still exert a strong influence on deposit formation, particularly for long storage periods. The fuel instability is manifested by the formation of insoluble products which play havoc with filters and nozzles of engines.

Oxidation is involved in the undesirable reactions as are fuel components containing hetero-atoms such as sulfur, nitrogen, and oxygen. More than free-radical autooxidation is involved, however, since typical free-radical antioxidants are ineffective in controlling this instability and can be deleterious (1). Further, degradation is increased by the presence of organic acids with the stronger acids exerting significant effects (2).

In this paper, we utilize several experimental techniques to characterize the insolubles as an aid in understanding the chemical processes which control the undesirable instability. The deposits examined include ones formed in stressed, undoped straight run/light cycle oil (SR/LCO) blends and in similar blends to which acids were added.

EXPERIMENTAL TECHNIQUES AND PROCEDURES

LCO and SR from a US Gulf Coast refinery were blended in a 20/80 ratio. The samples were stressed under accelerated conditions of 80 degC for 7 or 14 days, equivalent to 1 to 2 yrs at ambient conditions. Suspended products of instability were removed by filtration and products adhering to the stressing flask were removed with gum solvent. After evaporation of the solvent, the filterable and adherent insolubles were dried in a vacuum oven at 75 degC. The acids used as dopants were dodecylbenzene sulfonic acid (DBSA), chloroacetic acid (CA), and p-t-butyl thiophenol (PBTP).

Elemental analyses of the insolubles were done by Galbraith Laboratories, Knoxville, TN. Stressed and unstressed fuel blends and deposits were titrated in a non-aqueous solvent with approximately 0.04 N alcoholic KOH. X-Ray Photoelectron

Spectroscopy (XPS) analysis was conducted at the Naval Research Laboratory, Washington, DC and Field Ionization Mass Spectrometry (FIMS) was performed at SRI International, Menlo Park, CA.

EXPERIMENTAL RESULTS

Elemental Analysis. Table I lists the results of elemental analysis of various deposits from the stress tests. The carbon, hydrogen, and oxygen contents were similar for the insolubles from all samples. Nitrogen was lower for the sample derived from the fuel doped with p-t-butyl thiophenol. Sulfur was significantly higher for the blends doped with sulfur compounds, both the DBSA and the PBTP. All of these concentrations fall within the range observed for insoluble material derived from other storage stability experiments. The low H/C ratio (0.9 - 1.0) along with the high nitrogen, sulfur, and oxygen values support the view that hetero-aromatic compounds are major participants in insolubles formation. Chlorine was found in the insoluble sample derived from the fuel blend containing 0.01 M chloroacetic acid. Insufficient sample was available to do the other elements for this sample.

Titration Curves. Non-aqueous titrations of the stressed and unstressed liquid fuels gives useful information on the disposition of the added acids. Typical curves are shown for the sulfonic acid in Figure 1 and for thiophenol in Figure 2. The fuel blends for these titrations were not the same as the stress test samples but the same observations apply. The titrations in Figures 1 and 2 were done on different instruments which used opposite polarity conventions. The titration curve for unstressed DBSA exhibits a very high initial emf compared to the fuel blank. This is characteristic of strong acids such as sulfonic acids. The inflection point for neutralization of the strong acid is about +100 mv. The initial emf for the stressed DBSA is still high but the curve demonstrates that much of the DBSA is not available in the fuel after stress.

The titration curve for thiophenol shows that most of this weak acid has reacted during the stress period. Further, the initial emf has shifted from +120 mv to -220 mv. This is indicative of the presence of a very strong acid, sulfonic acid. Although the titer for strong acid is low, a definite quantity is present.

In addition to titration of the stressed and unstressed fuel blends, the solid sediments formed during the stress were subjected to non-aqueous titration. Strong acid was found in the sediments from the DBSA and PBTP doped samples.

XPS Analysis. This spectroscopic analysis was applied to the solids, both filterable and adherent, formed in the 80 degC stress. This technique affords good qualitative information but is not completely quantitative at low (<1%) levels of atomic %. This is due to electrical charging of the specimen in the high vacuum. Data for a typical analysis of insolubles is shown in Table II. The information is tabulated as atom % as opposed to weight % for Table I. This fact plus the fact that hydrogen is not determined

by XPS explains most of the differences between the results in Tables I and II.

Chlorine was detected only in the CA doped sample but just above the noise level. Sulfur is enhanced in the sulfur doped samples. XPS can distinguish between different valence states of atoms. This was particularly helpful in examining the sulfur composition. As Table III shows, reduced and oxidized forms of sulfur were found in these insoluble sediments. It is noteworthy, however, that the oxidized form predominates in the samples doped with the sulfonic acid and the thiophenol.

FIMS Analysis. This mass spectroscopic method affords a molecular weight pattern for a sample. The solids were pyrolyzed on a temperature-programmed probe in the inlet of the instrument. Further description and use of this technique will be detailed in another paper of this symposium. The highlights of FIMS application to the doped samples are as follows:

- (a) Major peak at 326 mass units for DBSA doped fuel;
- DBSA mol. wt. is 326
- (b) Major peaks at 166, 214, and 330 for PBTP doped fuel;
- PBTP mol. wt. is 166, PBTP dimer mol. wt. is 330, and p-t-butyl benzene sulfonic acid mol. wt. is 214
- (c) No peaks specific to CA were found in the insolubles from fuel doped with this acid

DISCUSSION

A test for material balance was made for the added acids. This was accomplished by non-aqueous titrations of the unstressed liquid fuel, the stressed liquid fuel, the filtration rinses, and the insolubles dissolved in titration solvent (1 part toluene to 1 part isopropyl alcohol). The petroleum ether rinses contained minute amounts of acid, only slightly more than the solvent blank. Table IV itemizes the balance for DBSA. A significant amount of strong acid was found in the insolubles, at least for the samples to which 1.0 mmol/L of DBSA was added. The acid concentration in the liquid fuel after stress and filtration was definitely lower than in the unstressed fuel. In fact, the amount of insolubles formed increases linearly with the decrease in DBSA concentration. Some of the DBSA could not be accounted for.

Added p-t-butyl thiophenol reacts rapidly at 80 degC and is 90% gone in two weeks. Most of this is probably oxidized to the disulfide.(3) Thus, PBTP and its products cannot be tracked by acid titration. However, a small amount of strong acid is found in the stressed fuel and in the insolubles. Two % of the thiol is found as strong acid in the stressed fuel and one % is found in the insolubles. Thus about 3 % of the thiol is oxidized all the way to a sulfonic acid.

The results on the material balance for chloroacetic acid were mixed. In one fuel the titer on the stressed, filtered fuel was similar to that for the unstressed material. In another fuel, 75 to 95 % of the titratable CA was lost from the liquid fuel after stress. Less than one % of this loss could be accounted for as titratable CA in the insolubles. Bound

(non-titratable) chloride could account for less than one % of the loss (1.2 % Cl in the insolubles x 8 mg/100 mL total insolubles for a fuel blend doped with 6.0 mmol/L of CA).

The overall thrust of the data on DBSA demonstrates that it is an active participant in insolubles formation for the SR/LCO distillate fuel blend. The fact that DBSA is present in the insolubles as titratable strong acid and the fact that the reaction occurs fairly quickly (2 to 5 days at 80 degC to attain a plateau for total insolubles (4)) indicates that the sulfonic acid is involved in salt formation. Corroborating evidence for this viewpoint comes from XPS, which found significant concentrations of sulfur in the oxidized form in the sediment from a DBSA doped fuel blend. The FIMS mol. wt. profile exhibited a large peak at 326, the mass of DBSA, another finding that supports the presence of DBSA in the solid formed during stress.

The earlier theory that acids act as catalysts for forming deposits in SR/LCO blends on the basis of their hydrogen ion concentration (2) must be modified, at least for DBSA. It would appear that DBSA operates in a dual role: (a) acid catalyst for deposit forming reactions and (b) direct participation in insolubles formation by salt formation.

PBTP participates in deposit formation by first oxidizing to p-t-butylbenzene sulfonic acid. This acid can then behave like DBSA, acting in the dual role of acid catalyst and active participant in forming insoluble salts. Only a small fraction of the PBTP converts to acid but the high reactivity of the acid makes it effective at low concentrations. The XPS and FIMS data support the incorporation of the acid in the deposits but direct addition of the thiol to olefins cannot be excluded.

The role of chloroacetic acid in deposit formation cannot be clearly defined on the basis of current knowledge. A theory from earlier work (2), which suggested that CA was acting as an acidic catalyst for deposit formation, may have to be modified.

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TABLE I
Elemental Analysis of Fuel Deposits

Dopant and Conc.	Percent Element							Total
	C	H	N	S	O	Cl	Ash	
None*	77.75	6.08	2.59	1.93	9.38	--	2.24	99.97
DBSA 0.001 M	76.99	6.44	2.53	3.84	9.26	--	0.98	100.04
PBTP 0.03 M	76.86	6.48	1.61	4.42	10.03	--	0.41	99.81
CA 0.01 M	--	--	--	--	--	1.22	--	--

*Deposit formed at ambient temperature. Other deposits formed at 80 degC, two weeks stress.

TABLE II
Percent Atomic Composition of Insolubles by XPS*

Dopant and Conc.	C	O	N	S	Cl
None	79.5	16.5	2.6	1.4	--
DBSA 0.001 M	75.5	18.7	2.9	2.8	--
PBTP 0.03 M	80.5	15.2	1.7	2.5	--
CA	77.0	18.9	2.1	1.3	0.3

*Insolubles formed in 80 degC stress for two weeks
Gulf Coast blend: 20% LCO in SR

TABLE III
Percent Atomic Concentrations of Two Different
Types of Sulfur by XPS

<u>Dopant and Conc.</u>	<u>Reduced Sulfur</u>	<u>Oxidized Sulfur</u>	<u>Total Sulfur</u>
None	0.5	0.9	1.4
DBSA 0.001 M	0.9	1.8	2.8
PBTP 0.03 M	0.6	1.9	2.5
CA 0.01 M	0.6	0.7	1.3

TABLE IV
DBSA Material Balance

<u>Stress</u>	<u>DBSA in Fuel</u>				<u>DBSA in Insolubles</u>	<u>DBSA Deficit</u>
	<u>DBSA Added</u>	<u>Before Stress</u>	<u>After Stress</u>			
80 degC 7 days	-0-	0.00	0.08		0.003	--
80 degC 7 days	1.00	0.96	0.71		0.12	0.13
80 degC 7 days	0.30	0.32	0.17		0.02	0.12
80 degC 14 days	1.00	0.84	0.68		0.15	0.01

DBSA Concentration in mmol/L

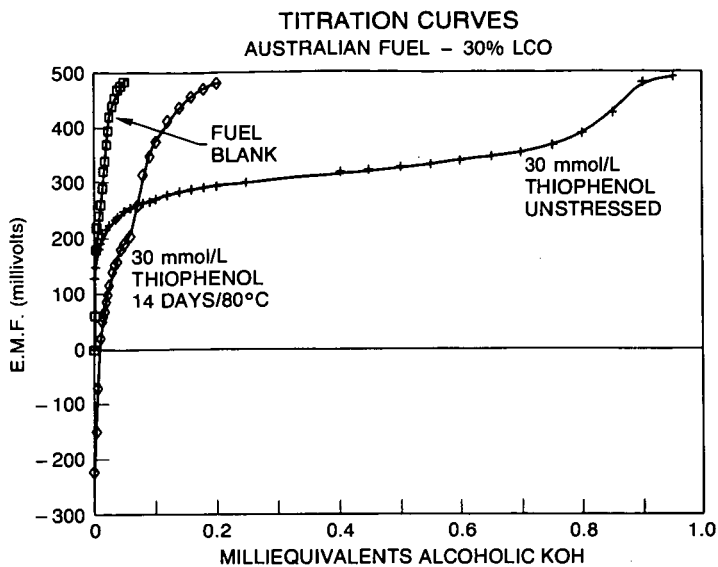


FIGURE 1.

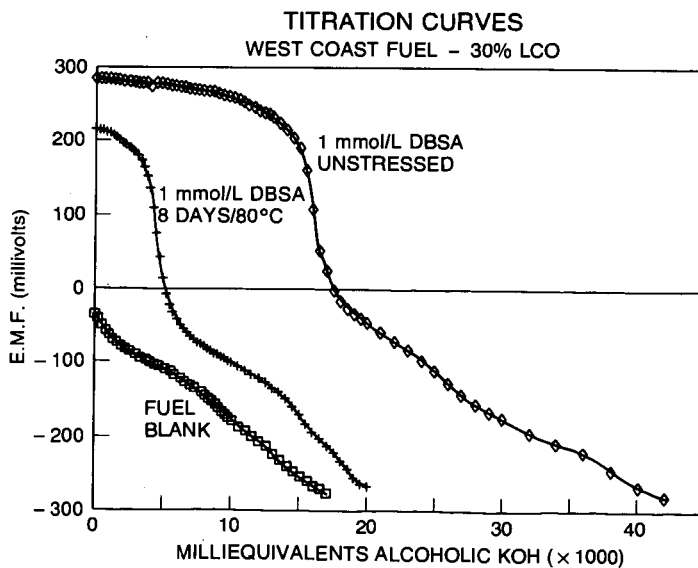


FIGURE 2.

FIELD IONIZATION MASS SPECTROMETRIC ANALYSIS OF SEDIMENTS FROM DIESELS DOPED WITH STRONG ACIDS

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KEYWORDS: Storage Stability, Adherent Gums, Deposits, FIMS, Sulfonic acids.

ABSTRACT

Filtered sediments formed in Texas diesel containing light cycle oil under ambient conditions and upon accelerated ageing at 80 °C for two weeks with added dodecylbenzenesulfonic acid (DBSA) or chloroacetic acid were examined by pyrolysis-field ionization mass spectrometry (Py-FIMS). During the analysis over 50% of the sediment was devolatilized. The spectra showed very similar profiles and correspondence between most prominent peaks indicating that doping with these acids does not drastically alter the chemistry of sediment formation, but merely accelerates the natural ageing. Sediments formed under accelerated ageing of the diesel doped with *p*-*t*-butylthiophenol again showed a similar spectrum as well as peaks for the oxidized products of the dopant, namely di-*p*-*t*-butylphenyl disulfide and *p*-*t*-butylbenzenesulfonic acid, thereby supporting the suggestion that sediment formation is an acid-catalyzed process and that sulfonic acids or other acids are formed by autoxidation of the fuel. Py-FIMS analysis of the adherent gum formed in the thiol-doped fuel gave a spectrum almost identical to that of the filtered sediment confirming their similar chemical nature.

INTRODUCTION

Storage of fuels often results in the formation of deposits that cause problems with filtration and pumping of the fuels. Furthermore, some soluble gum is also formed that subsequently forms deposits on the hot engine parts causing additional problems. Numerous tests have been developed to predict the tendency of a fuel to form deposits.(1) Often, these tests require stressing the fuel at elevated temperatures, and the relevancy of such tests to storage conditions is not clear. Studies have also been conducted with dopants (2, 3), but again it is unclear whether the deposits formed in the presence of the dopant are the same as those formed under storage. An improved chemical understanding of the nature and causes of deposit formation is clearly needed. Chemical characterization of the sediments is valuable, because the agents responsible for their formation may be present at extremely low concentration in the fuel, but will necessarily be concentrated in the sediments.

We have previously shown that pyrolysis-field ionization mass spectrometry (Py-FIMS) is very useful in characterizing the deposits formed during storage of fuels.(4,5) We have found that there are a few patterns that repeat in the spectra for sediments from a variety of sources and that the filtered sediments and adherent insoluble gums are very similar in chemical nature with the sediments being enriched in the benzologs of the components in the gum. We also showed that sediments from fuels with dopants such as 2,5-dimethylpyrrole (DMP) are completely different from that observed for undoped fuels; the sediment was largely comprised of DMP-derived materials. This result illustrates the possible dangers associated with studying accelerated aging using dopants and the need to characterize the sediments to ensure that the chemistry being examined is relevant to the native system.

We now wish to report results obtained from a variety of deposits obtained with fuels doped with strong acids or their precursors. The accompanying paper by Hazlett and Schreifels

(6) describes the aging experiments and the analysis of sediments by other techniques, such as titration with alkali and XPS, while this paper focuses on the analysis of the deposits by Py-FIMS.

EXPERIMENTAL

Accelerated Aging. A 20/80 blend of a light cycle oil with straight run diesel was aged at 80°C for 7 (or 14) days. Insoluble sediment formed in the fuel under ambient storage was also examined as an appropriate control. The dopants used in this study were: (1) a sample of dodecylbenzenesulfonic acid (DBSA), (2) *p*-t-butylthiophenol (PBTP), and (3) chloroacetic acid. The sediments were collected by filtration through glass fiber filters and the adherent gums were dissolved in a 1:1:1 (vol) mixture of toluene, acetone, and methanol, transferred to a small vial and the solvent evaporated.

Pyrolysis/Field Ionization Mass Spectrometry (Py/FIMS). The technique of field ionization (FI) consists of passing vapors of the material to be analyzed through a region of intense electric field.(7) This mild technique for ionization results in the formation of only the molecular ions for most compounds, and its nonfragmenting nature makes it particularly useful for analyzing complex mixtures. The FIMS system used in this study has been described elsewhere.(8) It consists of an activated tantalum foil field ionizer interfaced with a 60° magnetic sector mass analyzer and a PDP 11/23 computer for data acquisition and processing. Approximately 50 µg of the sample is introduced via a heatable direct insertion probe. Mass spectral data of the evolving volatiles are collected by repeatedly scanning the magnet over a preset range while the sample is gradually heated from the initial temperature (sometimes as low as -78°C) to approximately 500°C. At the end of the run, the sample holder is retrieved and weighed to determine the fraction that was devolatilized during the analysis. All the samples examined in this study were devolatilized to about 60% during analysis. For a given sample, many spectra are collected, each representing a certain range of temperature. The individual spectra are added to obtain a spectrum of the total volatiles and produce a thermal evolution profile of total volatiles as well as of any given mass peak.

RESULTS AND DISCUSSION

The Py-FIMS analysis of the adherent gum from ambient aging of the fuel gave the spectrum shown in Figure 1. It shows the characteristic groups of peaks corresponding to monomers, dimers, and trimers extending over the mass range 100 to 700 amu. The spectrum contains major peaks at *m/z* 131, 145, and 159. These features are in accord with those found in our previous investigations.(4,5) The peaks at *m/z* 131, 145, and 159 have been assigned to methylindole and its homologs (9-11).

Effect of Dodecylbenzenesulfonic Acid. Figure 2 shows the Py-FIMS of the filtered sediment formed upon stressing the fuel at 80°C for 7 days with DBSA as a dopant. The most intense peaks are seen at *m/z* 298, 312, and 326. Parent ion due to DBSA would appear at *m/z* 326, and we were puzzled to see the peaks at 312 and 298, which correspond to successive loss of methylene. The FI-mass spectrum of the DBSA sample also gave the peaks at *m/z* 312 and 298 in addition to the peak at *m/z* 326 and it appears that the particular sample of dodecylbenzenesulfonic is actually a mixture decyl-, undecyl-, and dodecyl- benzenesulfonic acids. The Py-FIMS of the deposit gave peaks at *m/z* 131, 145, and 159 and shows the general features of filtered sediments from undoped fuels (5) including relatively prominent peaks at *m/z* 181, 195, and 209 corresponding to the benzologs of methylindole and its homologs. On the basis of this information, we can surmise that DBSA does not drastically alter the chemistry of sediment formation but promotes the reactions that occur in undoped sediments. To the extent that DBSA is seen in the sediments as a prominent constituent, it must also contribute to insolubles formation. Whether this DBSA is present in the insolubles merely due to adduction or due to the formation of insoluble salts cannot be discerned at present.

Effect of *p*-t-butylthiophenol. Py-FIMS of the sediment obtained from doping the fuel with PBTP is shown in Figure 3. The spectrum is similar to the one for the sediment from the DBSA-doped fuel except that instead of the peaks due to the DBSA sample there are prominent peaks at *m/z* 166, 214, and 330. The peak at *m/z* 166 corresponds to PBTP itself and that at 330 to the corresponding disulfide, an expected product of oxidation. The peak at *m/z* 214 corresponds to *p*-t-butylbenzenesulfonic acid, and this observation lends support to the hypothesis that insolubles formed during storage are a result of acid-catalyzed chemistry, and that the acids are

themselves a product of autoxidation.(6) There is an additional prominent peak at m/z 185, which remains a mystery.

Effect of Chloroacetic Acid. Once again, the Py-FIMS of the sediment from the fuel doped with chloroacetic acid displays general features similar to those for the other sediments. Peaks due to chloroacetic acid (m/z 94 and 96) are absent and it appears that this acid is not adducted into the insoluble sediment. The absence of chloroacetic acid in the sediment would also suggest that salt formation is probably not the reason for the presence of other acids in the sediments, however, Cl was detected in the sediment by XPS (6) and we cannot draw any firm conclusions regarding the mechanism of dopant adduction at the present moment.

CONCLUSION

Pyrolysis-FIMS is a useful technique for characterizing fuel deposits. In this study, we showed that the nature of the deposits formed by doping the fuel with DBSA or chloroacetic acid is similar to that formed in undoped sediments. Substantial amounts of the deposits were devolatilized during the analysis ensuring that the data do not result from an insignificant part of the deposit. Oxidation of *p*-*t*-butylthiophenol results in the formation of *o*/*p*-*t*-butylbenzenesulfonic acid in addition to the disulfide. The sulfonic acid then catalyzes formation of insolubles.

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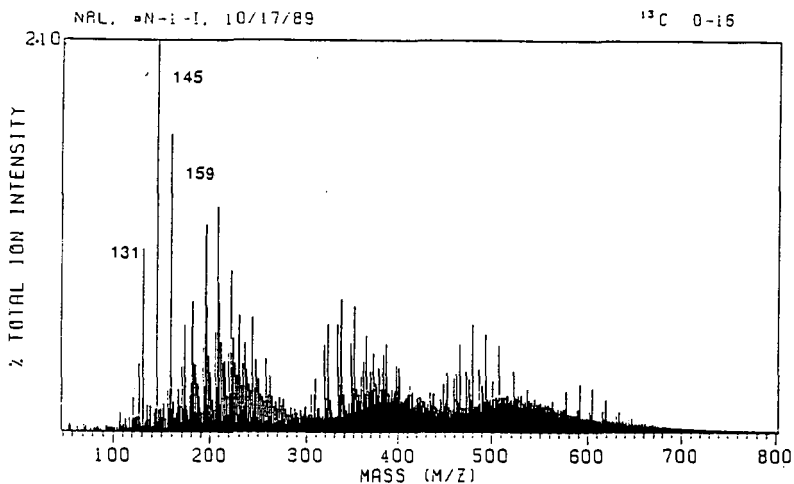


Figure 1. Py-FIMS of insoluble adherent gum from ambient aging of a 20/80 blend of light cycle oil and straight-run diesel.

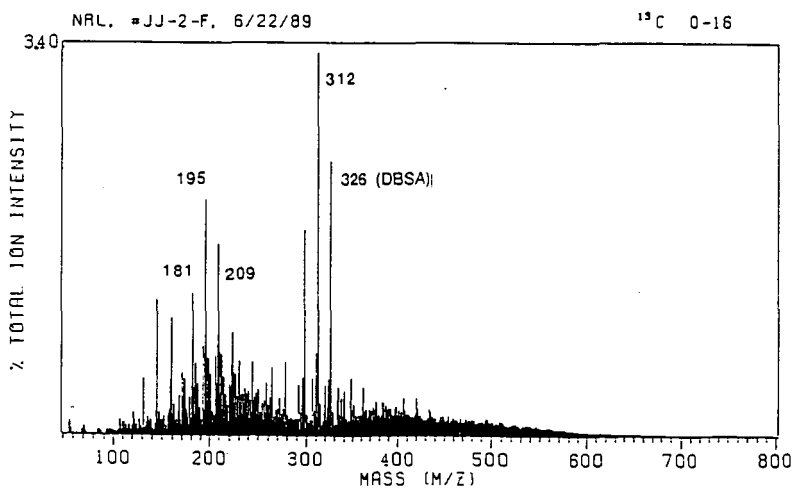


Figure 2. Py-FIMS of filtered sediment from accelerated aging at 80°C for 7 days of a 20/80 blend of light cycle oil and straight-run diesel doped with dodecylbenzenesulfonic acid.

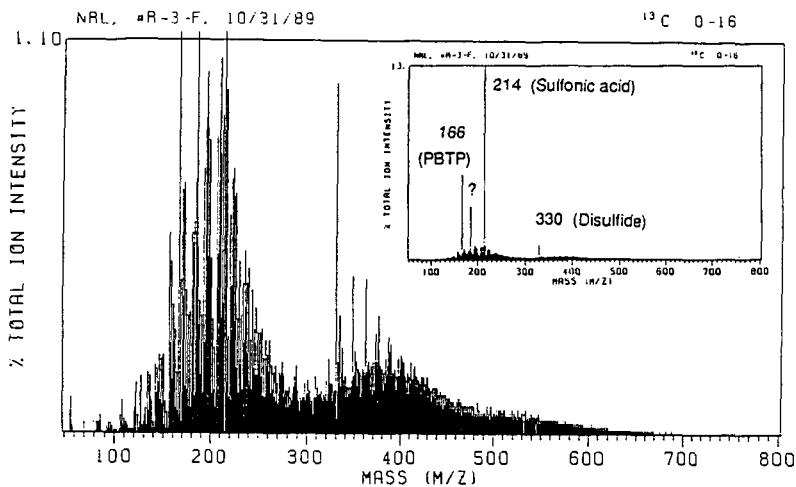


Figure 3. Py-FIMS of filtered sediment from accelerated aging at 80°C for 7 days of a 20/80 blend of light cycle oil and straight-run diesel doped with *p*-t-butythiophenol. (Inset: Same spectrum with increased vertical scale.)

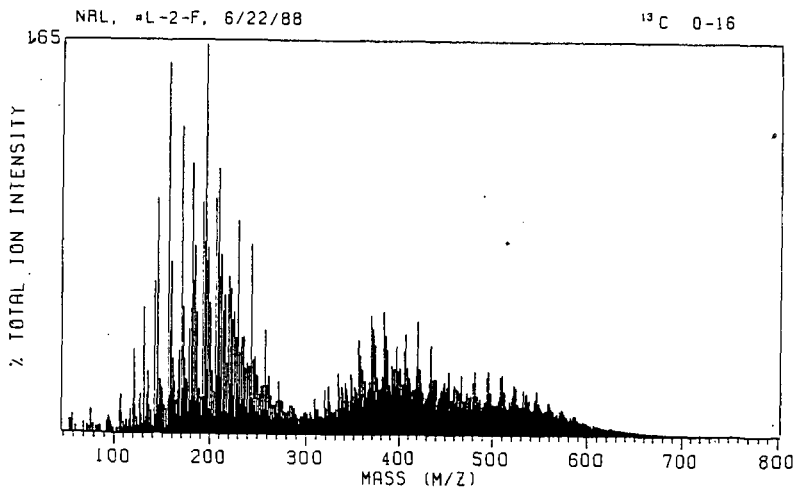


Figure 4. Py-FIMS of filtered sediment from accelerated aging at 80°C for 7 days of a 20/80 blend of light cycle oil and straight-run diesel doped with chloroacetic acid.

**THE MECHANISMS OF $\text{Fe}(\text{acac})_3$ AND $\text{Cu}(\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_{11})_2$
CATALYZED OXIDATION OF TETRAHYDROCARBAZOLE. IMPLICATIONS FOR
THE LONG TERM STORAGE STABILITY OF MIDDLE DISTILLATE FUELS.**

By

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INTRODUCTION

Pedley et al.^{1,2} have recently implicated alkylindoles in the chemical reactions which are responsible for the promotion of sediment and color body formation in an unstable diesel fuel (90% North Sea derived straight run/ 10% catalytically cracked) during sixteen months of ambient storage. In addition, Dorbon and Bernasconi³ have monitored the change in relative concentration of nitrogen compounds (indoles, carbazoles, and anilines) in four different LCO's upon aging (ASTM D4625: 43°C/12wks) and have reported the relative concentration of alkylindoles decreases to the greatest extent during aging.

Control of sediment and color body formation in unstable middle distillates during ambient storage has become an intractable problem. For example, it has been reported that two different commercial additive packages (composed of antioxidant, dispersant and metal deactivator) were ineffective in stabilizing two different unstable diesel fuels during ambient storage¹. The stabilization of middle distillates by catalytic hydrogenation to remove problematic indole nitrogen compounds is generally expensive owing to the high temperature and hydrogen pressure needed to effect denitrogenation⁴.

It is our belief that the ineffectiveness of commercial additive packages to sufficiently stabilize unstable diesel fuels during ambient storage is due to lack of understanding of the complex and fundamental chemistry involved in fuel oxidation. Consequently, we have initiated a research program directed at providing a greater understanding of the chemistry involved in low temperature middle distillate oxidation⁵. Herein, we report results of a model study of the $\text{Fe}(\text{acac})_3$ and $\text{Cu}(\text{O}_2\text{R})_2$ catalyzed oxidation of tetrahydrocarbazole (I, Figure 1), a representative alkylindole.

RESULTS AND DISCUSSIONS

In 1939, Beer et al.⁶ reported that while trying to recrystallize various tetrahydrocarbazole derivatives, good yields of tetrahydrocarbazole hydroperoxide derivatives were isolated. In 1950, Beer et al.⁷ reported that the structure of these hydroperoxides were that of the corresponding 1,2,3,4-tetrahydro-11-hydroperoxycarbazolenines (II, Figure 1). Subsequent studies revealed that the facile autoxidation of tetrahydrocarbazole derivatives is a general phenomenon and that the mechanism of this process involves a classical peroxy radical chain.⁸ Beer et al.⁷ and Witkop⁹, have also reported that in the presence of reducing agents or alkoxide, tetrahydrocarbazole hydroperoxides (THCHP) (II, Figure 1) are converted into the corresponding 1,2,3,4-tetrahydro-11-hydrocarbazolenine which can rearrange to the corresponding spiro-[cyclopentane-1,2'-V-indoxyl] (compound III, IV, respectively, Figure 1). In addition, Witkop and Patrick⁹ have reported that in the presence of polar solvents or acids, THCHP rearranges to 8,9-benzcyclononadi-2,7-one (V, Figure 1).

We have confirmed all of the above mentioned results and wish to emphasize that in the presence of a suitable chain breaking-donor (CB-D) antioxidant (BHT, Vitamin E, etc.) solutions of tetrahydrocarbazole are oxidatively stable. However, when trace amounts of either $\text{Cu}(\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)_2$ or $\text{Fe}(\text{acac})_3$ are added, THC is slowly oxidized (in the presence of CB-D antioxidants).

Based upon TLC analysis after the metal catalyzed THC oxidation, THCHP and all of the THCHP degradation products previously mentioned are present. Apparently the presence of the Cu and Fe complexes catalyze the formation of THCHP via a nonperoxy radical chain mechanism.

In Table 1 is reported the effect of addition of two copper deactivators upon the rate of the copper catalyzed THC oxidation. Both deactivators result in a suppression in the rate of oxidation. For instance, in the presence of the better deactivator, N,N'-bis(salicylidene)1,2-diaminopropane, the rate of THC oxidation is about 1/3 of rate in the absence of this deactivator.

We wish to report the following additional observations on the $\text{Fe}(\text{acac})_3$ and $\text{Cu}(\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)_2$ catalyzed THC oxidation:

- i) Table 2 and 3 reveal the metal catalyzed THC oxidation can occur even when a large concentration of a CB-D antioxidant is present. This observation suggests the mechanisms for these reactions doesn't involve a classical peroxy radical chain.

- ii) In addition, Table 2 and 3 reveal a different rate response in the presence of different concentrations of a CB-D antioxidant. This suggests that the mechanisms for the iron and copper catalyzed oxidations are different.
- iii) In Table 4 the rate of a typical copper catalyzed THC oxidation is compared with the rate of an identical reaction in which some tetrahydrocarbazole hydroperoxide (THCHP) was added at the start of the reaction. The observation of similar rates for these reactions additionally suggests that the mechanisms for this reaction is not a classical peroxy radical chain (lack of chain-branching).
- iv) In Table 5 is reported rate data for THC oxidation, as function of THC concentration and metal complex concentration. This data suggests the iron catalyzed reaction is first order in THC and .1 order in iron while the copper oxidation is 1/2 order in THC while .3 order in copper.

CONCLUSION

Pedley et al.² have proposed a mechanism which accounts for the involvement of indoles in the formation of sediment and color bodies during ambient aging of an unstable North Sea derived diesel fuel containing catalytically cracked stock. In this mechanism, indoles in the presence of conjugated ketones and acid, result in electrophilic aromatic substitution of the indole with concomitant increase in indole molecular weight and color body formation owing to formation of indolic chromophore. Protonation of the resultant indole results in sediment formation.

The results of this work suggest that alkylindoles can promote fuel degradation in a capacity other than that observed by Pedley et al.^{1,2}. In the presence of trace amounts of Fe(acac)₃ and Cu(O₂CCH₂CH₂CH₂C₆H₁₁), tetrahydrocarbazole is oxidized, initially forming tetrahydrocarbazole hydroperoxide (THCHP). A very high concentration of Vitamin E was necessary to completely inhibit the Cu catalyzed reaction while the Fe catalyzed reaction was not totally inhibited.

We have shown that in the absence of catalytically active metal ions and in the presence of CB-D antioxidant THC is oxidatively stable. This observation suggests that more efficient metal deactivators need to be developed in order to counter the effect of alkylindole oxidation upon middle distillate degradation.

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ACKNOWLEDGMENT

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FIGURE 1

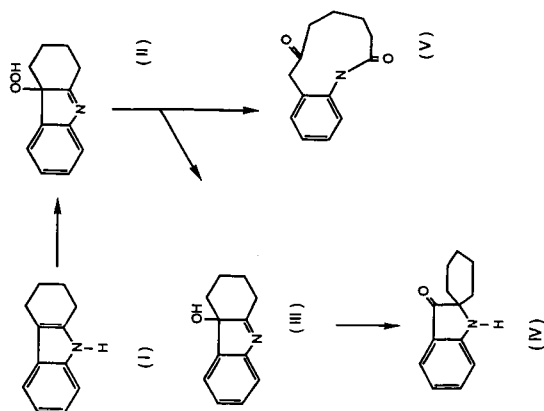


Table 1*

Effect of N,N bis[salicylidene]1,3-propanediamine and N,N'-disalicylidene-1,2-propanediamine on the Rate of THC Oxidation

Conditions: 2.34×10^{-2} M THC; 2.34×10^{-2} M vitamin E; 50°C ; 9.95×10^{-5} Cu²⁺ cyclohexane butyrate; 50mls 3:1 Heptane-Toluene

MDA	Equivalents of Salicylidene (wrt Cu ²⁺)	rate (moles/l min) ($\times 10^6$)
1,3	0	10.4
1,3	1.0	5.6
1,3	1.5	5.5
1,2	0	10.4
1,2	1.5	2.8

* Solutions of purified THC, vitamin E, metal and tridecane (GLC internal standard) were prepared in the appropriate solvent mixtures. The solutions were placed in a constant temperature water bath and bubbled with O₂. Aliquots were taken prior to O₂ bubbling and approximately two hours after bubbling. The aliquots were analyzed for THC decomposition using GLC.

Table 2

Relationship between Vitamin E Concentration and the Rate of
THC Oxidation

conditions:

2.23×10^{-2} M THC/ 1.42×10^{-4} M Fe₃+acac/ 50°C/ 50mls 3:1
Heptane-Toluene

Vitamin E (moles/l)	rate (moles/l min) (10^{-6})
0.58×10^{-2}	17.0
1.16×10^{-2}	10.9
2.34×10^{-2}	7.1
4.67×10^{-2}	5.9
9.34×10^{-2}	4.8
14.01×10^{-2}	4.0

Table 3

Relationship between Vitamin E Concentration and the Rate of
THC Oxidation

conditions:

2.34×10^{-2} M THC/ 1.99×10^{-3} M Cu₂+(cyclohexane butyrate)/40°C/
50mls 3:1 Heptane-Toluene

Vitamin E (moles/l)	rate (moles/l min) (10^{-6})
1.16×10^{-2}	121.0
2.34×10^{-2}	8.34
4.67×10^{-2}	9.55
7.00×10^{-2}	9.23
9.34×10^{-2}	NR
11.67×10^{-2}	NR
16.35×10^{-2}	NR

Table 4

Effect of the addition of THCHP on the rate of THC oxidation

conditions:

2.34×10^{-2} M THC/ 1.99×10^{-5} M Cu²⁺(cyclohexane butyrate)/ 40°C
/ 50mls 3:1 Heptane-Toluene/ 2.34×10^{-2} M vitamin E

THCHP (mg)	rate (moles/l min) (10^{-6})
0 (control)	8.34
10	8.42

Table 5

Determination of Order in THC and Metal

Determination of order in THC with Fe³⁺+acac

Conditions: 1.0 eq. Vitamin E (wrt THC) ; 1.41×10^{-4} M
Fe³⁺+acac ; 50°C ; 50mls 3:1 heptane -toluene

THC (moles/l)	rate (moles/l min) (E-6)
0.58×10^{-2}	1.55
1.16×10^{-2}	4.1
1.75×10^{-2}	5.5
2.34×10^{-2}	7.1
4.68×10^{-2}	12.6
7.01×10^{-2}	15.4

Table 5

Determination of order in Fe3+acac

Conditions: 2.34×10^{-2} M THC; 2.34×10^{-2} M Vitamin E ;
50°C ; 50mls 3:1 heptane -toluene

Fe3+acac (moles/l)	rate (moles/l min) (E-6)
2.83×10^{-5}	5.9
1.41×10^{-4}	7.1

Determination of order in THC with Cu2+ cyclohexane butyrate

Conditions: 1.0 eq. Vitamin E (wrt THC) ; 9.95×10^{-5} M Cu2+
cyclohexane butyrate; 50°C ; 50mls 3:1 heptane -
toluene

THC (moles/l)	rate (moles/l min) (E-6)
1.16×10^{-2}	6.75
2.34×10^{-2}	9.65

Determination of order in Cu2+ cyclohexane butyrate

Conditions: 2.34×10^{-2} M THC; 2.34×10^{-2} M Vitamin E ;
50°C ; 50mls 3:1 heptane -toluene

Cu2+ (moles/l)	rate (moles/l min) (E-6)
1.99×10^{-3}	6.9
4.97×10^{-3}	9.7
9.95×10^{-3}	10.6
19.89×10^{-3}	14.0

**WHAT ARE SOLUBLE MACROMOLECULAR
OXIDATIVELY REACTIVE SPECIES (SMORS)?**

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INTRODUCTION

The search for diesel fuel components which can be linked to insolubles or sludge formation as a product of oxidative aging has led to some interesting new findings recently. Pre-filtered fuel which is oxidatively aged under accelerated conditions which simulate one to two years of ambient storage is filtered to determine the product insolubles formed. If the filtrate is then subjected to size exclusion chromatography (SEC), no intermediate molecular weight or size components are observed. If the fuel-insoluble product which has been removed by filtration is solubilized and subjected to identical SEC analysis, a broad peak centered on 600 to 800 daltons is the principle chromatographic feature. If the aged fuel is not filtered and simply dissolved in SEC mobile phase, numerous species of varying molecular size can be detected in the range of 150-1000 daltons. The higher molecular weight features of these chromatograms are very similar to the fuel-insoluble product after aging; the lower molecular weight features are what one would expect if oxidation and condensation reactions of fuel monomeric species were consecutively reacting to form the ultimate fuel-insoluble high molecular weight product. However, the absence of these intermediate molecular weight species in the filtered fuel leads to the unconventional conclusion that oxidation of fuel monomeric species is not responsible for sludge formation.

A second related finding is that after extraction of unstable diesel fuels and light cycle oils (LCOs) with methanol, the tendency of these stocks to form insoluble sediment upon oxidative aging is greatly reduced (1). This finding is illustrated in Table I, where four blends of 30% LCO in straight run from four separate refineries are subjected to aging in the low pressure reactor at 90° C for 24 hours at 100 psig oxygen. The pass/fail criterion is about 6 mg/100 ml. The samples were extracted with strong aqueous base and with methanol (described in experimental section below). The methanol extracted fuels are greatly stabilized in all cases regardless of the relative stabilities of the unextracted control samples.

Table II illustrates the effect of methanol extraction on either the straight run distillate or LCO portion used to make up the blend. It is readily apparent that the insolubles precursors are primarily associated with the LCO portion. More remarkable is the fact that the isolated methanol extract can be dissolved in a hydrocarbon solvent (which by itself does not form insolubles under the LPR aging conditions) and after aging an insoluble sediment can

be isolated. In two of the three blends (B-3 and B-4) a remarkable mass balance is achieved in that the sediment from the extracted blend plus the sediment from the methanol extract in solvent equals the sediment in the unextracted blend. For B-5 the methanol extract in the solvent formed even more sediment than the original fuel blend. These results indicate clearly that the precursors to fuel-insoluble sediment are very efficiently extracted into the methanol.

Attempts were made to analyze the methanol extract from a range of unstable LCOs in order to determine the gas chromatographable monomeric fuel components responsible for insoluble sediment formation. It was not possible to correlate any particular compound or compound class present in the relatively easily analyzed methanol extract as being responsible for the product insoluble sediment.

Evaporating the methanol extracts to dryness led to an intractable tar. Attempts to weigh the tar were abandoned due to the impossibility of achieving constant weights. If this tar is carefully precipitated with hexane, it is possible to isolate a dark solid material which is filterable on a 1.2 micron glass fiber filter. This solid material may be washed with hexane, dried and weighed. The material has been named soluble macromolecular oxidatively reactive species (SMORS) (2). Typical values for SMORS from a variety of straight runs and LCOs are given in Tables III and IV. Again it is apparent that the reactive LCO generally contains SMORS at varying levels, as determined by a simple methanol extraction and hexane precipitation. This led to the observation illustrated in Figure 1 that the weight of SMORS in any catalytically cracked LCO was linearly related to that LCOs tendency to form fuel-insoluble sludge after oxidative aging.

This paper presents additional information about the physical and chemical nature of the SMORS and the nature of their role in blends with straight run distillate streams. The possible use of the simple SMORS determination as a substitute for traditional accelerated storage stability tests in certain cases will also be discussed.

EXPERIMENTAL

All of the fuels and blend stocks fell within ASTM D975 diesel fuel number 2 specification requirements. Most of the much more stringent U.S. Navy Distillate Diesel Fuel specifications (MIL F 16884) were also met by almost all of the fuels and blend stocks. The fuel code used throughout the tables is: SR = straight run distillate, LCO = catalytically cracked light cycle oil, B = a blend of SR + LCO, a number following any of the letter codes refers to a different refinery source. Fuel sources were primarily US in origin but several European samples are included.

The storage stability test utilized is described in detail elsewhere (3) and utilized the so-called low pressure reactor (LPR) at 90° C and 100 psig oxygen for various periods of time.

All fuel samples are first pre-filtered using Gelman Type A/E glass fiber filters before either extraction or aging. The methanol extraction procedure uses fuel/methanol volumes of 100 ml/40 ml in a 250 ml separatory funnel. The two phases are vigorously shaken for about 90 seconds and the system allowed to settle until good separation occurs, typically 2-5 minutes. The fuel layer is then drawn off and discarded and the methanol phase is decanted into a 125 ml brown borosilicate bottle which is immersed to the neck in a boiling water bath to evaporate the methanol. In order to achieve good repeatable quantitation, it is absolutely essential that all the methanol is driven off because of the very high solubility of the hexane insoluble fraction of interest in methanol. After evaporation the sample is allowed to cool to room temperature. About 50 ml of filtered ACS reagent grade hexanes are then added to the bottle and any hexane insoluble material is precipitated. The sample is then vacuum filtered through a pre-weighed 47 mm Gelman type A/E glass fiber filter in a Buchner funnel, rinsed well with hexane and allowed to dry thoroughly before weighing again. If constant weights are not achieved with ambient air drying the samples may be oven dried at about 60° C for an hour. When it is desirable to recover the solid material from the filter for subsequent analysis a 0.8 micron Millipore type AA or a Nylon 66 filter may be substituted for the glass fiber filter, and a Millipore filtering apparatus for the funnel.

RESULTS AND DISCUSSION

The SMORS can be quantitatively isolated either before or after an accelerated aging test (on a separate aliquot if before the aging test). It is important to note that the SMORS solids should not be confused with the product insoluble sediment solids. The product insoluble sediment is removed from the post aged fuel by filtration and then the post aged filtered fuel may be extracted to determine the SMORS solids after aging.

Size exclusion chromatograms of representative samples of the SMORS solids both before and after stress tests were obtained. The chief characteristic was a molecular weight peak of about 700 to 900 daltons. Qualitatively and quantitatively the chromatograms of the SMORS were similar for all LCOs both before and after aging. In addition, the physical appearance and solubility characteristics of the SMORS was similar for all of the LCOs.

The nature of the SMORS led to their descriptive acronym. They are soluble in diesel fuels. They are macromolecular, that is, they are much greater average molecular weight than the diesel fuel range. They are oxidatively reactive species, that is, they are apparently primarily responsible for the oxidative formation of sludge products in the fuel.

The SMORS are not just precursors to sludge formation in catalytically cracked LCOs but are apparently prerequisites in a necessary but not sufficient regard. The examination of SMORS in many diesel fuels has led us to propose the values in Table V as a possible compositional requirement governing storage stability. If a fuel contains a high (>30 mg/100 ml) concentration of SMORS, problem levels of sludge formation are inevitable at ambient conditions in less than 6 months. If the concentration of SMORS is very low (<1 mg/100 ml), irregardless of fuel source, composition and refining process no fuel related sludge formation will take place even after very long storage at ambient. At intermediate levels (1 to 30 mg/100 ml) it would be advisable to further scrutinize the fuel by running a realistic accelerated stability test.

The physical appearance and nature of SMORS is very intriguing. The fact that they are particulate and filterable on a 0.8 to 1.2 micron filter indicate that they are physically similar to the product insoluble sediment. It has been suggested by Chertkov, et al (4) that the product solid phase is not formed by the oxidation of fuel components but is present in the fuel in the form of a colloidal system. Oxidation of the fuel leads to the destruction of this colloidal system and precipitation of the solid phase. They believe that this higher molecular weight material already existent in the fuel is responsible for sludge formation in both diesel and jet fuel. Further they claim that this material should be similar to petroleum asphaltenes except in their much higher oxygen incorporation.

In an effort to extend our understanding of the chemical nature of the SMORS, we investigated the effect of several straight run streams on several LCOs. A high acid (SR-5A) and a low acid (SR-11) fuel was blended into various LCOs and the SMORS yields determined before and after a 24 hour LPR test. The product insoluble sediment was also determined. Table VI illustrates two representative LCOs. The effect of the straight runs regardless of their acid content is not simply that of diluent to the SMORS. For either LCO we would calculate about 14 mg on the basis of dilution for the 40% v/v case and 7 mg for the 20% v/v LCO case. In both cases (pre-stressed) we obtain about double the calculated weight of SMORS. As usual, with either LCO the straight run blends give higher amounts of insolubles than the starting LCO itself. It is quite interesting that the low acid SR yields almost double the high acid SR blend for either LCO. Yet the effect on SMORS is invariant regardless of acid level before or after aging.

Since the addition of the straight run seems to favor the partition of SMORS into the initial methanol extract, we next investigated the effect of a pure hydrocarbon model for the SR on the effect of SMORS yields. Hexadecane was chosen as the diluent and the effect on LCO-5 is given in Table VII. The effect of the pure hydrocarbon diluent is to drive the partition coefficient even more into the initial methanol extract. It is interesting to note that even when the dilute blends are aged about twice the insoluble

sediment is formed over the neat LCO case. The pre-stressed SMORS expressed on a 100 ml LCO basis are 30 to 50% increased in the dilution range of 20 to 80% v/v hexadecane.

This leads us to consider not so much the nature of the SR or diluent phase as controlling the various amounts of product insoluble sediment as the nature of our original determination of SMORS in the blends. In blends, it becomes of greatest importance to maximize the partition coefficient of the initial extraction into methanol. This, then, would allow us to determine if the SMORS (however isolated) are the primary controlling reagents in product insolubles formation.

Since the effect of strong acid addition to blends of catalytically cracked LCO in SR exerts such a pronounced effect on the insoluble sediment production of these fuels (5), we examined the effect of such acid addition on the yields of pre-aged SMORS. Table VIII illustrates our results for LCO-14 with and without the addition of 0.010 M chloroacetic acid. Remarkably the SMORS yields were increased about four fold. This concentration of this acid addition to LCO/SR blends generally has the effect of increasing the product sediment yields by about somewhat less than ten fold. Since Tables VI and VII show the effect of increasing the SMORS yields simply by adding an SR diluent, the effect of adding acids to SR/LCO blends would be predicted to increase the SMORS yields somewhat more than the four fold increase of added acids to the neat LCO. The effect of added acid to the LCO may indeed be nothing more than the destruction of an already existent colloidal dispersion in the cracked LCO material, leading to the production of greater amounts of insoluble sediment.

CONCLUSIONS

The original scheme for isolating this new class of material from fuel (the SMORS), has been extended in the current work. The effect of SR or pure hydrocarbon dilution of the LCO on SMORS yields reveals that the original levels determined in the neat LCOs themselves is probably on the low end. This leads to a desire to maximize the partition coefficient into the initial extractant phase. The addition of an organic acid at low concentration has been shown to have the desired effect and will be pursued using additional acids and blends of LCO/SR in addition to other LCOs.

SMORS are important pre-requisites and precursors of sludge formation in aged diesel fuels. This makes the further refinement of the physical isolation method of SMORS an important area of study. In addition, the further detailed characterization of the SMORS may aid fuel producers and users in minimizing the deleterious impact of this material by selectively controlling and realistically predicting its effects.

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TABLE I. Results of KOH and Methanol Extraction on Insolubles Formation. Aging test is LPR at 90°C, 24 hours, 100 psig oxygen. Pass/Fail criterion is 6 mg/100 ml.

Fuel Blend	Mg insolubles/100 ml		
	Control	KOH Ext.	MeOH Ext.
B-2	1.4	2.0	0.8
B-3	9.4	9.2	2.2
B-4	6.8	3.8	2.4
B-5	11.4	10.6	2.0

TABLE II. Effect of Methanol Extraction on 3 Reactive Fuels. Aging as in Table I. Series 1 = unextracted 70/30 blends. Series 2 = 35 ml extracted SR blended with 15 ml LCO. Series 3 = extracted 70/30 blends (MeOH). Series 4 = 35 ml SR blended with 15 ml extracted LCO. Series 5 = MeOH fraction from series 3 suspended in 25/75 butylbenzene/dodecane.

Fuel Blend	Mg insolubles/100 ml		
	B-3	B-4	B-5
Series 1	10.2	8.2	12.6
Series 2	10.8	7.2	14.6
Series 3	4.0	3.2	2.2
Series 4	5.0	3.2	4.4
Series 5	6.6	5.0	19.6

TABLE III. Weight of Solids Isolated from the Hexane-insoluble Fraction of the Methanol Extract of 7 SR Fuel Stocks. Aging as in Table I.

<u>Fuel Code</u>	<u>Hexane Insolubles (mg/100 ml)</u>		<u>Insol. Sed. (mg/100 ml)</u>
	<u>Pre-stress</u>	<u>Post-stress</u>	
SR-3	0.0	ND	0.0
SR-4	0.1	0.1	0.0
SR-5A	0.7	2.0	0.6
SR-5B	0.0	0.6	0.4
SR-11	0.0	0.1	0.1
SR-12	0.2	ND	0.0
SR-13	0.1	0.1	0.3

TABLE IV. Weight of Solids Isolated from the Hexane-insoluble Fraction of the Methanol Extract of 8 Cracked LCOs and 1 Blended Diesel Fuel. Aging as in Table I.

<u>Fuel Code</u>	<u>Hexane Insolubles (mg/100 ml)</u>		<u>Insol. Sed. (mg/100 ml)</u>
	<u>Pre-stress</u>	<u>Post-stress</u>	
LCO-1	112	116	27.0
LCO-2	14	17	3.3
LCO-3	53	63	13.0
LCO-4	27	40	3.4
LCO-5	92	114	20.0
LCO-12	1	14	4.7
LCO-13	2	101	33.0
LCO-14	2	58	4.0
B-3	14	18	8.2

TABLE V. Use of SMORS (mg/100 ml) as Simple Compositional Test for Predicting Storage Stability of any Mid-distillate Fuel.

<u>Weight of SMORS (mg/100 ml)</u>	<u>Insoluble Forming Tendency</u>	<u>Action</u>
<1	Fuel has indefinite storage life	No accelerated stability test needed
<30 and >1	Fuel stability generally worse at higher SMORS levels	Accelerated stability test required
>30	Fuel will degrade significantly in less than 6 months	No accelerated stability test needed

TABLE VI. The effect of various Straight Run (SR) Distillate Blends in LCOs on SMORS yields. All values in mg/100 ml of fuel.

Volume Ratio SR/LCO	LCO ID	Pre-Stress SMORS		Post-Stress SMORS		Insol. Sed. Post Stress	
		Hi Acid SR-5A	Lo Acid SR-11	Hi Acid SR-5A	Lo Acid SR-11	High Acid	Low Acid
0/100	LCO-14	34	34	60	60	3	3
60/40	LCO-14	25	27	35	35	6	10
80/20	LCO-14	15	15	23	19	5	8
0/100	LCO-4	34	34	57	57	2	2
60/40	LCO-4	31	30	35	37	5	10
80/20	LCO-4	17	15	12	19	4	7

TABLE VII. Effect of Hexadecane as Diluent on SMORS Yields of an LCO. Aging conditions as in Table I.

Volume Ratio LCO-5/Hexadec.	mg SMORS per 100 ml LCO	Insol. Sed. (mg/100 ml)
100/0	96	11
80/20	129	23
50/50	148	20
20/80	147	23
0/100	0	0

TABLE VIII. Effect of 0.010 M Chloroacetic Acid on Pre-stressed SMORS Yields.

Sample	SMORS (mg/100 ml)
LCO-14	6
LCO-14 + Acid	23

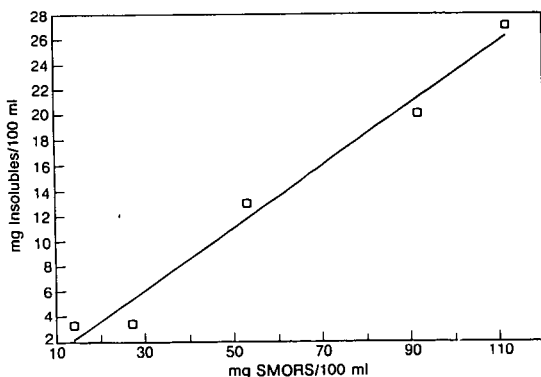


Figure 1. Correlation of weights of pre-stressed methanol extractable/hexane insolubles (SMORS) for 5 LCO samples with corresponding weight of product insolubles. See Table I for aging conditions. Standard error for each axis=±15%.

**SYMPOSIUM ON THE
STABILITY AND OXIDATION CHEMISTRY OF MIDDLE DISTILLATE FUELS
PRESENTED BEFORE THE DIVISIONS OF FUELS AND PETROLEUM CHEMISTRY
AMERICAN CHEMICAL SOCIETY
WASHINGTON, DC, MEETING, AUGUST 26-31, 1990**

A FUEL STABILITY STUDY: TOTAL INSOLUBLES AS A FUNCTION OF TIME

By

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INTRODUCTION

The David Taylor Research Center, in cooperation with the Naval Research Laboratory (NRL) plus contract laboratories, has been studying the effectiveness of stability additives in Naval Distillate fuels since 1983. Initial studies of the antioxidants permitted in Naval Distillate showed that not all the antioxidants are equally effective and that some might even be detrimental.⁽¹⁾ Later work with nine commercial additives in a number of fuel stocks showed that two of the additives were consistently more effective than any of the other seven additives.⁽²⁾

The first test of commercial additives was run on a fuel stock containing 40% light cycle oil. When a low level of insolubles (about 0.6 mg/100 mL of fuel) was obtained, it was considered too low to obtain a good evaluation of the effectiveness of additives. We therefore investigated the effect of stress times greater than the 16 hours prescribed in the ASTM D2274 procedure. Subsequently, we conducted such time studies on a total of 21 fuel stocks. This paper summarizes the results of those studies and discusses the implications of our findings.

MATERIALS AND PROCEDURES

Materials - The 21 fuel stocks used in the study included one straight run (SR) stock, 4 light cycle oils (LCO), 10 SR/LCO blends containing 30%(vol) LCO, 3 containing 40%, 2 containing 15%, and a blend of high sulfur, heavy diesel fuel in a CAT 1H fuel. The stocks were obtained by NIPER (National Institute for Petroleum and Energy Research) from Gulf coast, west coast, east coast, and mid-continent refineries. Table 1 shows available ranges of properties measured on the stocks (not all stocks).

Procedures - The ASTM D2274 test for the oxidation stability of distillate fuel by the accelerated method was used, with modifications.⁽³⁾ The primary modification was the use of residence times both less than and greater than the 16 hours at 95°C specified by the test method. The maximum time used was 96 hours. In a second modification, we cleaned the apparatus without using chromic acid solution. In a third modification, we evaporated adherent gum solvent by other than the jet gum procedure.

RESULTS AND DISCUSSION

The 21 time response curves of total insolubles as a function of residence, or stress time, are shown in Figures 1 through 5. They exhibit a tendency toward an S-shaped curve consisting of an induction period, followed by a period of rapid formation of total insolubles, and finally a leveling off to some final value. The curve obtained with Fuel 30-10 (Figure 2) is the best example of this tendency. Sauer and coworkers⁽⁴⁾, using a somewhat different test procedure, published similar curves as long ago as 1958. Cooney and coworkers⁽⁵⁾, Hazlett and coworkers⁽¹⁾, and Westbrook and coworkers⁽⁶⁾ also obtained similar curves in 80°C bottle tests.

Various mechanisms have been proposed for the formation of insolubles in fuels. Sauer and coworkers⁽⁴⁾ suggested the side-chain oxidation of reactive compounds in a fuel to form hydroperoxides which then decomposed to form aldehydes; the aldehydes were postulated to react with other peroxides to form peroxyhemiacetals, which in turn decomposed to form condensed, esterified higher molecular weight products. They suggested a typical sediment molecule containing a pyrrolic structure.

Frankenfeld and coworkers⁽⁷⁾, from a study of dimethylpyrrole (DMP) in jet fuel, concluded that sedimentation appeared to be a free radical, autoxidative reaction involving a mechanism similar to that proposed by Sauer. They also concluded from a study of shale liquids that nitrogenous sediment formation in such liquids involves oxidative oligomerization of nitrogen compounds and that the neutral, heterocyclic compounds such as alkyl pyrroles and indoles appear to be especially reactive.

Hazlett and coworkers⁽⁸⁾ in a study of diesel fuels doped with DMP and stressed at 80°C, conducted elemental analyses, gas chromatographic analyses, and infrared spectroscopic examinations of the sediment. They remarked on the consistency of the elemental analyses on sediments from tests conducted under a wide variety of conditions. They found the atomic ratio of carbon to nitrogen was about 6:1 indicating the sediment was derived from the DMP.

The shape of the curves found in the current study is consistent with such past work. An induction period is consistent with the theory of consecutive reactions and the approach to a final value of total insolubles is consistent with the findings of an oligomerization with a specific chemical composition. We suggest that a few reactive species present in a fuel, primarily the reactive nitrogen compounds identified by Frankenfeld are involved in sediment formation. The rate at which such formation takes place, however, may be a function of the acidity and solvency of the system, of the presence of catalytic substances such as copper compounds, and of the presence of inhibitors, either naturally present or added.

Figures 1 - 5 also show the normal 16 hours of residence is frequently too early to catch the part of the curve where total insolubles increase at a fast rate. In most cases, the breakpoint has occurred by 20-24 hours. See, for example, the curves for Fuel 30-10 in Figure 2 and for LC-2 in Figure 3. The total insolubles produced in LC-2 by the end of 32 hours of residence time is 20-times the total insolubles produced in 16 hours.

Thus, the curves make us realize that no single-time test of short duration can be adequate for defining the behavior of a fuel in ambient storage. Rather, we need a test method that determines the induction period (the breakpoint time), the rate of increase of insolubles formation following the breakpoint, and the ultimate total insolubles formed after a long period of oxidative stability testing.

As a by-product of our time response program, we obtained some interesting data on the effect of light cycle oils (LCO) on the stability of straight run stocks. In two cases, we had available both the straight run stock and the LCO in addition to blends of 15%, 30%, and 40% LCO in the straight run. In the one case, we ran time response curves for the entire gamut of concentrations. The total insolubles obtained after 16 hours, 32 hours, and 40 hours of residence time are shown in Figure 6 as a function of the LCO concentration.

The lack of linearity of the curves in Figure 6 indicate that total insolubles obtained with the straight run stock and with the LCO are not additive. Addition of the more stable straight run stock to LCO does not provide a simple diluent effect. The chemistry responsible for this effect is not known, but it may be related to the acidity of the system, which some investigators, such as Hazlett⁽⁹⁾, postulate as having a catalytic effect on the reactions involved in insolubles formation.

We have one additional figure, a figure which shows the effect of pre-aging. Pre-aging was accomplished by sparging a fuel with air and then allowing the sample to sit for a month at ambient laboratory temperatures before running D2274-type tests. Figure 7 compares the time responses of the pre-aged fuel and of the same fuel prior to pre-aging. The pre-aged fuel started rapid formation of insolubles at a much earlier point in time than the unaged fuel. Beyond the point at which 1.5 mg of total insolubles per 100 mL of fuel have been formed, the two curves are essentially parallel. This indicates the rate of formation of new insolubles is the same for the pre-aged and unaged fuel.

We postulate that the pre-aging permitted the formation of intermediates which would normally be produced during the early stages of the D2274 test. Then, when the pre-aged fuel was tested by the D2274 procedure, the formation of the insolubles could start immediately. We further postulate that, once the intermediates have been formed, the further reaction to form total insolubles is the same in the two cases.

FINDINGS AND CONCLUSIONS

1. Time response curves of total insolubles vs. residence time have an S-shape if carried for a sufficient period, and the total insolubles level approaches an asymptotic value.

2. Single time stability tests are incapable of fully defining the stability characteristics of a fuel.

3. The blending of two fuel stocks may not result in sediment formation that is a linear function of the sediments produced by each fuel stock alone.

4. Pre-aging a fuel stock prior to determining its time response curve affected only the length of the induction period.

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TABLE 1
RANGES OF PROPERTIES OF STOCKS USED IN TIME STUDY

Property	30% Blends	40% Blends	LC Oils	Other Stocks
Density, kg/m ³	840 - 895	859 - 901	896 - 953	836 - 869
Viscosity, cSt	2.0 - 3.8	2.6 - 3.2	2.6 - 3.3	2.9 - 3.2
Distillation, °C				
IBP	144 - 223	180 - 221	213 - 224	198 - 217
10% Point	207 - 258	234 - 244	243 - 254	232 - 243
50% Point	232 - 292	270 - 283	269 - 283	267 - 283
90% Point	290 - 332	313 - 335	306 - 326	319 - 335
End Point	324 - 349	345 - 349	323 - 329	338 - 349
Cetane Index	38 - 49	36 - 48	23 - 37	44 - 54
Sulfur, %	0.2 - 0.8	0.2 - 0.9	0.3 - 1.0	0.3 - 0.6
Nitrogen, mg/L	43 - 266	44 - 246	61 - 428	25 - 151
TAN, mg KOH/g	.02 - .23	.02 - .15	.02 - .06	.04 - 0.25
Bromine No.	.23 - .43	.51 - 1.13	0.47	.12 - .47

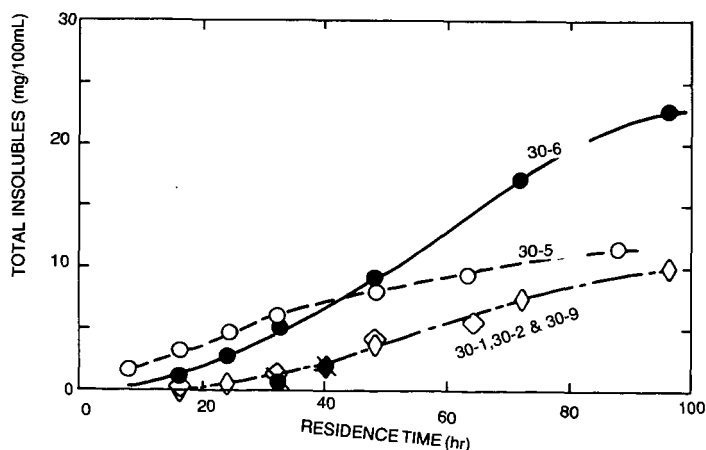


Fig. 1 - Time response curves for five fuels containing 30% LCO and 70% SR (Fuels 30-1, 30-2, 30-5, 30-6, and 30-9).

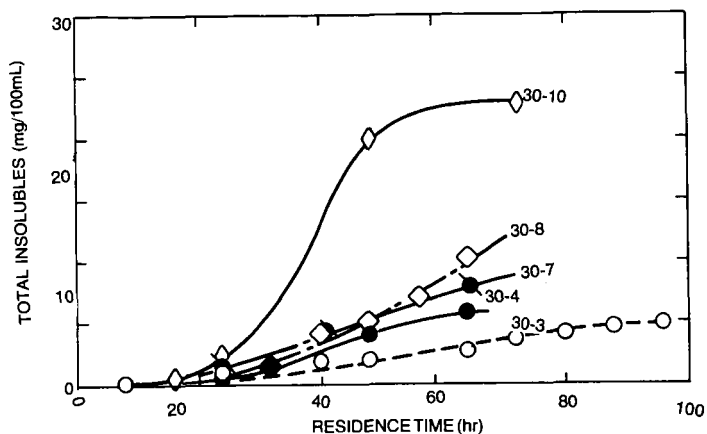


Fig. 2 - Time response curves for five fuels containing 30% LCO and 70% SR (Fuels 30-3, 30-4, 30-7, 30-8, and 30-10)

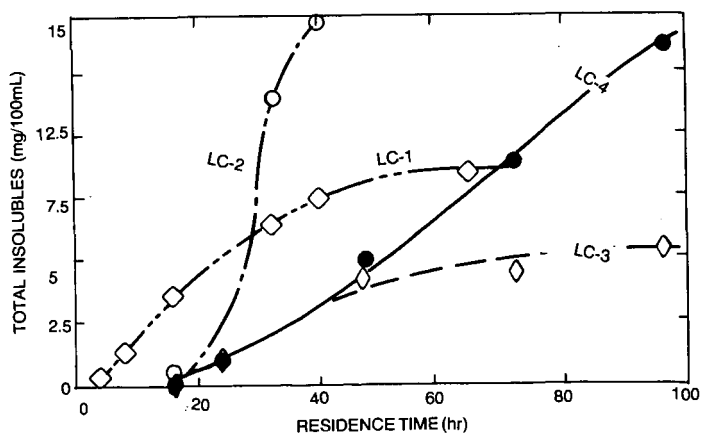


Fig. 3 - Time response curves for four light cycle oils

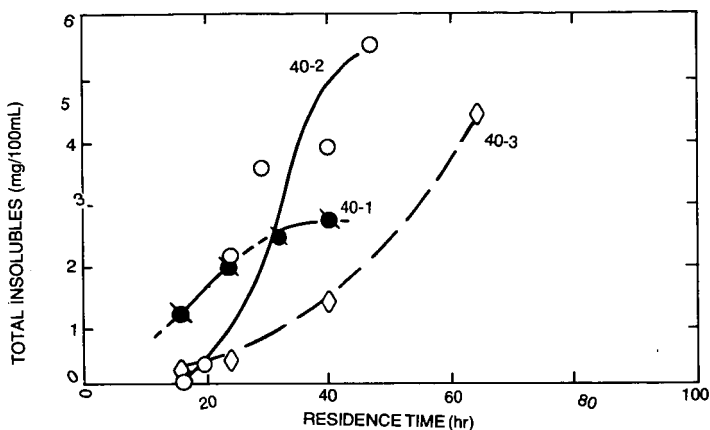


Fig 4 - Time response curves for three fuels containing 40% LCO and 60% SR.

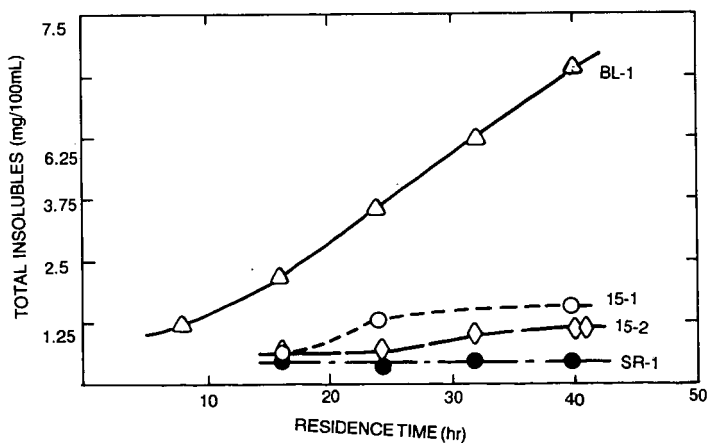


Fig. 5 - Time response curves for four miscellaneous fuels (Fuels 15-1 and 15-2 containing 15% LCO; straight run Fuel SR-1; and Fuel Blend BL-1, a high sulfur diesel fuel in CAT 1H fuel).

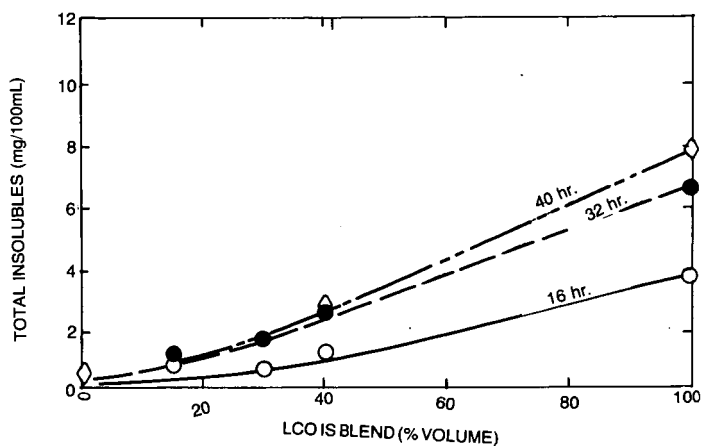


Fig. 6 - Curves showing effect of LCO concentration in straight run/light cycle oil blends on the total insolubles formed in 16 hours, in 32 hours, and in 40 hours of D2274-type stressing.

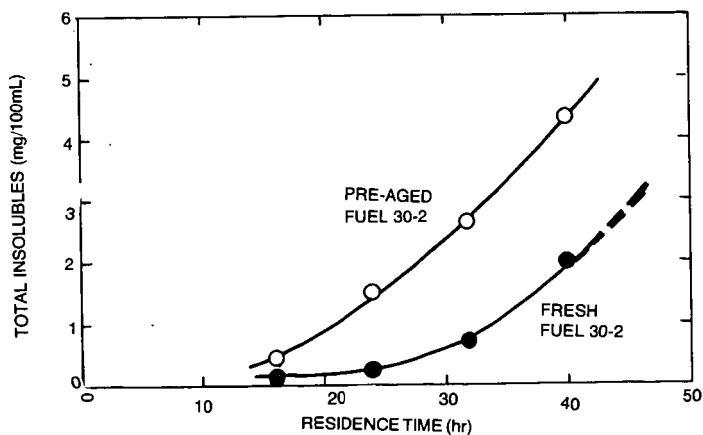


Fig. 7 - Time response curves for pre-aged and unaged Fuel 30-2; the effect of pre-aging on the formation of total insolubles.

STABILITY OF AUSTRALIAN AUTOMOTIVE DIESEL FUELS

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INTRODUCTION

The storage stability of automotive diesel (ADF) fuel can vary across a wide spectrum, depending principally on the properties of its parent crude oil and the refining processes employed in its production. Fuels with inadequate storage stability produce insoluble gums and organic particulates which result in engine operability problems due to blocked fuel filters. There is currently no precise definition of just what constitutes acceptable storage stability for automotive diesel fuel. As an approximate guide, a rate of formation of insolubles of 20 mg/L per year of ambient storage has been proposed as the maximum rate for 'stable' ADF.¹⁻³ The absence of an accelerated test which can reliably predict the storage stability of diesel fuels has contributed to the current unsatisfactory situation. However, a test developed by the US Naval Research Laboratory is showing considerable promise for satisfying this long-standing need.

RESULTS AND DISCUSSION

Stability of Australian ADFs The results of stability tests on 76 ADFs from the eight major Australian refineries are shown in Figure 1. These fuels were produced during the 15 month period from October 1987 to the end of December 1988. Most fuels were obtained during transfers of ADF from the refineries to terminal distribution tanks, so the fuels can be assumed to be less than one month old prior to being subjected to stability tests. The survey results in Figures 1 and 2 were obtained using the 43°C/13 week test, which simulates one year of storage at typical ambient temperatures. As discussed in the following section, this test is regarded as a reliable indicator of storage stability, and has recently been adopted as an ASTM Standard test method.

Figure 1 shows that the stabilities of Australian ADFs span a wide range. Of the 76 fuels tested, a majority (76%) yielded less than 10 mg/L of insolubles. A majority (67%) of those fuels which yielded insolubles >10 mg/L emanated from a single refinery, and all of the fuels with inadequate stability (>20 mg/L) came from that refinery. Figure 1 shows, however, that the same refinery produced batches of high stability ADF in addition to the low quality batches, resulting in average insolubles of 12 mg/L. This average level of insolubles is by far the highest of any of the eight refineries (see Figure 2). Three refineries consistently produced very high stability ADF, with average total insolubles <4 mg/L. The remaining four refineries produced ADF with average total insolubles of 6-7 mg/L, indicative of ADF with good storage stability quality.

From a similar though less extensive survey of Australian ADFs covering

the period 1982-86, it was concluded that Australian ADFs were exceptionally stable, and that ADF yielding more than 5 mg/L insolubles in the 43°C/13 week test was rarely produced by Australian refineries. The current survey shows a very different picture with approximately half of Australian ADF production yielding more than 5 mg/L of insolubles. However, judged by the <20 mg/L criterion for stable ADF, current Australian-produced ADFs (apart from refinery C) generally have high storage stability quality.

The very high stability observed in the 1982-86 period was attributed to the low heteroatom content of Gippsland Light (the principal crude feedstock for Australian refineries), and to the widespread use of diesel hydrotreating process or stabilizing additives. There have been many publications² warning that the stability of automotive diesel fuel must decline as refiners meet increasing ADF demands by inclusion of higher proportions of cracked blendstock (light cycle oil), and as refiners are forced to process crudes containing greater proportions of certain destabilizing heteroatom compounds. Furthermore, the stability of (untreated) cracked blendstock may have decreased as refiners direct heavier feedstocks to their cracking units. These trends are probably contributing to the lower storage stability revealed in the 1987-88 survey. Other factors may also have contributed. Some refiners may be seeking to reduce refining costs by reducing use of their highly effective but expensive hydrotreating units. This cost-saving approach is attractive because it has been demonstrated that storage stability can be achieved without hydrotreating, by careful selection of a stabilizing additive package.^{4,5} From results of the current survey of Australian ADFs, it is apparent that at least one refiner is either underdosing or making a poor selection from the range of commercially available stabilizing additives. Furthermore, an underlying cause for this situation may be the use of unreliable accelerated stability tests to assess the performance of commercially available additives.

Accelerated Stability Tests The formation of insoluble organic matter in diesel fuels during storage is the result of complex interactions among a range of reactive species in the fuel, and molecular oxygen. At least three classes of chemical reaction (eg oxidative gum formation, acid-base reactions and esterification) can occur.^{2,8,9} The more reactive compound classes include heteroatom compounds and olefins. Certain compounds eg alkyl pyrroles, indoles⁹ and thiophenols¹⁰ are known to be particularly potent destabilizers of diesel fuel. Recent years have seen a renewed interest in achieving a better understanding of the complex chemistry of diesel fuel degradation, leading to an improved understanding of the complex chemistry involved.^{11,12}

The complexity of the chemistry of diesel fuel degradation has been the principal barrier to the development of a reliable accelerated storage stability test. The methods used to accelerate the insoluble-forming reactions include higher temperature, higher oxygen concentration and copper catalysts. Certain insoluble-forming reactions, however, may be more sensitive to the accelerated reaction conditions. Hence, the overall chemistry occurring under the accelerated conditions may be quite different from that occurring under non-accelerated conditions viz. normal storage of ADF. Consequently, highly accelerated tests are likely to be the least reliable indicators of storage stability, unless they have been thoughtfully devised and carefully evaluated.

Based on American and European experience, there is general agreement that the mild acceleration involved in the 43°C/13 week storage stability test results in reliable assessment of storage stability at normal storage temperatures. Consequently, the American Society for Testing and Materials introduced the new standard test method ASTM D4625 "Distillate Fuel Storage Stability at 43°C" in 1988. For Australian ADFs, Figure 3 compares results from the 43°C/13 week ASTM test and one year storage of 700 mL samples in metal cans in a non-air conditioned shed in Brisbane, Australia (average temperature ≈25°C). While the experimental data show some scatter, it can be concluded that the quantity of insolubles formed during storage at ambient temperatures for one year is approximately equal to the quantity formed during 13 weeks at 43°C. Thus the 43°C/13 week test can be confidently employed for assessing the ambient storage stabilities of Australian ADFs.

Figure 4 shows the correlation between total insolubles formed in the more accelerated 80°C/7 day test and insolubles formed in the 43°C/13 week test, for a selection of Australian ADFs. The figure shows that the 80°C/7 day test can serve a useful predictive function for the more stable fuels, even though results do not correlate particularly well with results from the 43°C test. Those fuels which yielded less than 3 mg/L in the 80°C test also performed well in the 43°C test. However, fuels yielding 4-8 mg/L in the 80°C test yielded a very wide range of insolubles (3-32 mg/L) in the 43°C test. Hence, as a potential quality control test, the 80°C/7 day test shows inadequate correlation with the 43°C/13 week test if it is to be applied to fuels with a wide range of storage stabilities. Thus the acceleration of the processes of formation of filter-blocking insolubles has reduced the reliability of the accelerated test, even before the time required for the test has been shortened to the <24 hr period desirable for a refinery quality control test method.

Other studies involving attempts to accelerate ambient storage conditions by raising the temperature and shortening the test time suggest that 80°C/7 days may be much too severe to attempt a reasonable correlation to 43°C/13 week tests (Hardy et al, 1986). That work suggests that 80°C/4 to 5 day bottle tests should correlate much better with the 43°C/13 week tests for any given fuel. Unfortunately the precision of the test results obtained at 80°C/4 to 5 days is very poor and hence those conditions are not acceptable as a refinery quality control test for accelerated stability. Shortening the test time at 80°C below 4 days results in increasingly poor test precision or repeatability thus effectively barring the use of this test at the refinery.

One Australian refiner adopted an accelerated test based on a temperature of 100°C and the accelerating effect of soluble copper at a concentration of 10 mg/L. The test period of 2 h was short enough for the test to be used for quality control, and the test was used for acceptance/rejection purposes for ADF exchange between some Australian oil companies. Figure 5 shows that the test is clearly unsuitable for this application, even though there is a degree of correlation with the 43°C/13 week test. The problem is that some fuels which are stable (according to the <20 mg/L criterion for the 43°C/13 week test) are classed as unstable by the highly accelerated copper naphthenate test. Such a test is clearly unsuitable for quality control of large production batches of ADF, and in the light of evidence such as

presented in Figure 5, the test was abandoned in 1988. The possibility that similar situations may reoccur again highlights the need for a reliable short-term test for quality control of ADF storage stability.

While Figures 4 and 5 show that attempts to accelerate the formation of insolubles can result in unreliable storage stability tests, the combination of increased temperature and oxygen pressure may be more reliable. Figure 6 shows results for five US middle-distillate fuels, spanning a broad range of stability, when tested at 43°C for 18 weeks in atmospheric bottle tests and 43°C for 4 weeks at 100 psia oxygen. A linear least squares correlation gives $R^2 = 0.98$ for these two tests. The correlation between 43°C/4 weeks/100 psia and 80°C/64 hr/100 psia of oxygen is 0.97 for these same five fuels. This is a clear indication that a combination of increased temperature and increased oxygen pressure together should be quite useful for predicting ambient storage stability for most middle-distillate fuels.

The Oxygen Overpressure Stability Test A new oxygen overpressure method for predicting distillate fuel's tendency for forming deleterious fuel insolubles during ambient storage is rapid and precise and is predictive for up to 3 years of ambient conditions. For this test 100 mL samples of filtered fuel in 125 mL borosilicate bottles were placed in a low pressure reactor (LPR). The reactor was sealed and pressurized with 99.5% pure oxygen to 100 psig. The samples were stressed, while maintaining the oxygen pressure, under accelerated storage conditions for set temperatures and times. At the end of the stress period, the amount of filterable sediment and adherent sediment were determined gravimetrically and reported as total insoluble sediment weight. Samples were run in triplicate and the average values are reported in mg/100 mL.

Work at 43°C for up to 4 weeks at 100 psig (see Figure 6) and at 80°C for up to 64 hours at psia shows very good correlation with bottle tests done at 43°C (slight variation of ASTM D4625). In an attempt to make the test shorter, recent work has been done at 90°C for 16 hours at 100 psig for possible use as a new ASTM method.

Table 1 shows comparison gravimetric results for two accelerated storage stability tests using a variety of diesel fuels. Two of the fuels are blends of 30% cracked stock (LCO) and 70% straight run. One fuel is a blend of 30% diesel fuel containing 2% sulfur (HSD) and 70% straight run. The remaining fuels were US Naval Distillate fuels (NATO F-76). Very good correlation between the results of the lower temperature bottle tests and the oxygen overpressure tests is shown. When the pass/fail criteria at the bottom of the table is applied, it can be seen that, with the exception of one sample, the oxygen overpressure method correctly assessed the stability of these fuels when compared with the longer bottle tests. This fuel would be considered marginal by both methods.

This method has also been useful in assessing the relative effectiveness of middle-distillate fuel stabilizer (antioxidant) additives. Table 2 shows typical results for a slightly unstable fuel. The oxygen overpressure method correctly assessed the additive-free fuel in addition to evaluating the additives when compared to the lower temperature test. Additive 7 is a noteworthy exception when comparing the two test methods. This indicates the need to possibly extend the

test times of the 16 hour 100 psig test to exceed reaction induction times. Also, in two cases, additives 3 and 4, the 90°C test appears to be more severe than the 43°C test.

Figure 7 shows the gravimetric results obtained when the same six fuels, of various stabilities, were analyzed at NRL and at AMPOL using the oxygen overpressure method. Very good correlation between the results is shown, especially when it is considered that the samples were analyzed using reactors constructed separately at each of the labs. These results also show that the method has good reproducibility.

CONCLUSIONS

The storage stability of Australian automotive diesel fuels has decreased from the extremely high quality which existed five years ago. With the exception of one refinery, however, Australian refineries still produce ADF with good storage stability. Assessment of long-term storage stability by means of highly accelerated laboratory tests remains a challenge. Most highly accelerated tests have limited reliability when compared with the mildly accelerated 43°C/13 week test. The oxygen overpressure method, however, is showing promise of filling the long-standing need for a rapid, reliable test.

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TABLE 1. TOTAL INSOLUBLES (mg/L) FROM ACCELERATED STABILITY TESTS

Sample Description	43°C/18 wk Bottle Test	90°C/16 hr/100 psig LPR Test
30%LCO/70%SR (Refinery 1)	89	46
30%LCO/70%SR (Refinery 2)	60	38
30%HSD/70%SR (Refinery 3)	44	62
NATO F-76 (1)	39	39
(2)	5	7
(3)	7	13
(4)	11	7
(5)	12	14
Pass/Fail	40	30

TABLE 2. TOTAL INSOLUBLES (mg/L) FOR (30%LCO/70%SR) DIESEL FUEL FROM A U.S. GULF COAST REFINERY TREATED WITH VARIOUS STABILIZING ADDITIVES

Sample Description	43°C/18 wk Bottle Test	90°C/16 hr/100 psig LPR Test
2	19	7
3	28	38
4	39	52
9	43	31
6	45	28
8	47	24
1	52	34
5	56	31
7	56	14
Neat	62	45
Pass/Fail	40	30

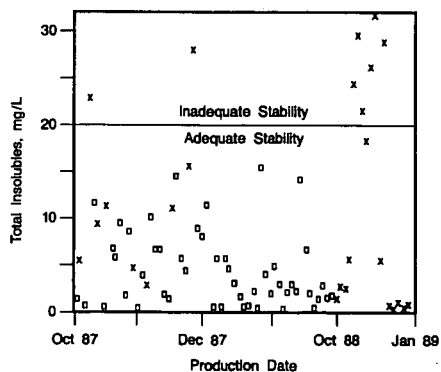


Figure 1. Total Insolubles Formed During Oven Storage at 43°C for 18 Weeks. Cross-Symbols - Refinery C; Square Symbols - Other Australian Refineries.

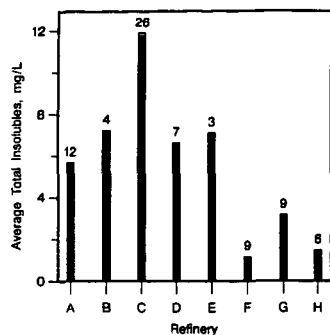


Figure 2. Average Insolubles from 13 Weeks at 43 °C for ADF from Australian Refineries. The Numbers of Samples Tested Are Indicated.

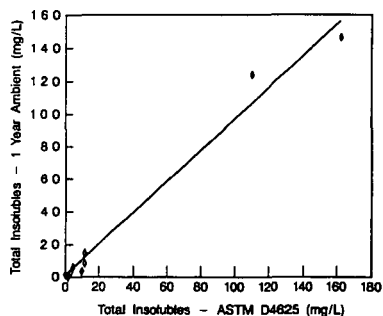


Figure 3. Correlation of Total Insolubles Formed During One Year at Ambient Temperatures and During 13 Weeks at 43 °C (ASTM D4625).

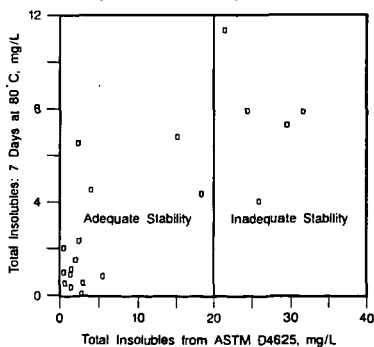


Figure 4. Correlation of Total Insolubles Formed During 7 Days at 80 °C and During 13 Weeks at 43 °C (ASTM D4625).

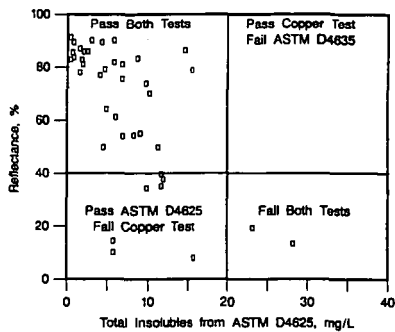


Figure 5. Correlation of a Stability Test Employing Copper as an Accelerating Agent with Insolubles Formed During 13 Weeks at 43°C.

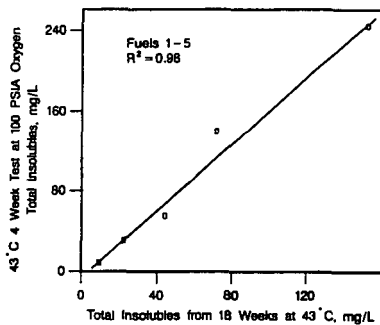


Figure 6. Comparison of 43°C/4 Week/100 PSIA O_2 Test Results with 43°C/18 Week Data.

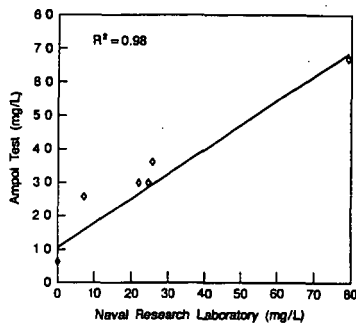


Figure 7. ASTM Round Robin Results for Oxygen Overpressure Stability Test (90°C/16 Hr/100 PSIG)

Assessment of the Oxygen Overpressure Test for Prediction of Middle Distillate Fuel Storage Stability

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ABSTRACT Gravimetric amounts of sediment produced by the oxygen overpressure test for ageing middle distillate fuels for 16 hours at 90°C with a pressure of oxygen of 794 kPa (100 psig) have been compared with that produced by ASTM D4625 conditions at 43°C for 13 weeks. Fifteen fuel blends comprising 30% light cycle oil or 30% hydrotreated light cycle oil were included in this study. Whereas approximately half of the fuel blends produced comparable amounts of sediments by the two procedures, there was no correlation overall for ranking fuels based on sediment produced. Comparison of gravimetric amounts of sediments produced by 12 months ambient ageing with that produced in the oxygen overpressure test of the ambient aged fuels again produced no correlation between the two procedures. The species separated by thin layer chromatography of the sediment produced in the oxygen overpressure test were compared with those produced under ASTM D4625 conditions. There was much similarity in the species observed for the standard oxygen overpressure conditions, but significant differences were noted as the temperature of stress used in the oxygen overpressure test was raised above 90°C. At the higher temperatures, brown species extending over all R_f values began to predominate in the thin layer chromatograms.

INTRODUCTION

World wide demand for middle distillate fuel continues to increase as at a greater rate than other fractions of the oil refinery barrel. This demand is being partly met by the greater use of cracking of the heavier distillation products and incorporation of this cracked stock in the form of light cycle oil (LCO) into automotive diesel fuel. The direct incorporation of LCO into automotive diesel fuel is one of the major, if not the most significant contributing factor, to the formation of insoluble particulate and gums on storage of the fuel.¹

With the decrease in fuel stability, the necessity for an accurate test to predict the storage stability of a distillate fuel is increased. Lower temperature bottle tests are generally the best indicators of storage stability and recently a 43°C test has been standardized as ASTM D4625. The length of time required to obtain significant amounts of sediment for reliable results by ASTM D4625 is a major drawback for quality control. The method of ASTM D2274 has been the most widely used rapid method for assessment of the fuel storage oxidative stability of a fuel.² However, it has been found that this test is a poor predictor for the storage stability of freshly refined fuel containing catalytically cracked stock.³ For many fuels, the amount of sediment produced in the 16 hour period at 95°C is too small to be measured accurately.⁴ Recently an oxygen overpressure technique has been proposed in which fuel is stressed for 16 hours at 90°C in an atmosphere of 794 kPa (100 psig) oxygen.³ This test has

the advantage that significant amounts of sediment were produced in a relatively short time period and good precision was obtained in replicates of gravimetric amounts of sediment.

For this oxygen overpressure technique to find widespread use as a predictive tool, it is necessary that it predicts the relative ambient storage stability of distillate fuels. This study was undertaken to correlate gravimetric amounts of sediment produced under both ambient and ASTM D4625 conditions with that of the oxygen overpressure technique. Reference fuels were chosen so as to include both freshly refined diesel fuel containing either thermally or catalytically cracked stock and aged commercial diesel fuels. Opportunity was taken of an associated study⁵ to compare the species present in sediments from oxygen overpressure conditions with those produced from the ASTM D4625 procedure. Correlation of both gravimetric amounts of sediment and chemical species present in the sediment would add to the confidence with which the oxygen overpressure technique could be used for predicting the relative storage stability of distillate fuels.

The role of reactions between alkylindoles and phenalene species to sediment formation in the reference distillate fuels is presented elsewhere.⁵ In this presentation, the initial concentration of alkylindoles in the reference fuels is considered in relation to the species observed in thin layer chromatograms of sediments produced by the oxygen overpressure technique and in correlations between total amounts of sediment produced by oxygen overpressure conditions and the ASTM D4625 procedure.

EXPERIMENTAL

Samples from automotive distillate refinery streams of straight run distillate (SRD), light cycle oil (LCO) and hydrotreated light cycle oil (HTLCO) were obtained directly from Australian refineries. All samples were reported to have being produced in less than one week of receipt. LCO was from catalytic crackers for all refineries except one, which has a thermal cracking unit. Samples were either blended upon receipt for immediate commencement of the ageing trial or stored as unblended components at -12°C. Experimental fuels were prepared by mixing 30% (volume/volume) LCO or HTLCO with SRD and filtering the mixture through glass fibre membranes (Millipore AP40) immediately prior to use. For all experimental samples, except FG1 and FG2 of Table 3, the sample components originated in the same refinery. Samples FG1 and FG2 were mixtures of 30% LCO and 30% HTLCO respectively from refinery F with SRD from refinery G.

Oxygen overpressure measurements were determined in the single bomb apparatus of ASTM D942 using 75 ml of fuel in 100 ml lipless borosilicate containers. The bomb containing the fuel sample was purged three times with 99.5% purity oxygen prior to being placed in a thermostated liquid bath which maintained the temperature to within 0.1°C. After being immersed in the bath for 15 minutes, the pressure was adjusted to 794 kPa (100 psig). During most runs the oxygen pressure decreased by 40-50 kPa. Upon completion of a run, the bomb was removed from the liquid bath and allowed to cool to ambient temperature prior to sediment determinations.

Suspended particulate matter in the samples was determined by filtration of the fuel through duplicate pre-weighed glass fibre membranes (Millipore AP40). Adhered insolubles were determined by rinsing the containers with triple solvent (equal amounts of toluene, acetone and methanol) and hot plate evaporation of the solvent in disposable aluminium dishes and algebraic subtraction of a blank evaporation of equivalent amounts of solvent. Total sediment was the sum of the suspended particulate matter and the adhered insolubles. Data shown in the tables is the average of two duplicate fuel sample determinations.

The 13 week 43°C ageing was carried out according to the method of ASTM D4625 using 1 litre borosilicate containers thermostated in an air oven. The automotive diesel fuel samples listed in Table 4 were obtained directly from retail commercial outlets or sampled directly from user storage tanks in Northern Australia. Although the specific origin of this fuel is unknown, it is most likely that a significant proportion originated from refineries in Singapore. The fuel was stored in 1 litre plastic containers at ambient temperatures for 12 months after collection of the samples prior to the measurements. Total sediment measurements as described above were determined for the fuel prior to its use for the oxygen overpressure measurements.

Thin layer chromatograms of the sediments were obtained by dissolving the sediment directly from the glass fibre membranes with 10% methanol in dichloromethane. This solvent was then used as the mobile phase with a silica gel stationary phase. Alkylindoles were determined in the fuel samples after concentration of the polar species on a small column of silica followed by elution with dichloromethane. This solvent was evaporated with a gentle stream of nitrogen and the residue dissolved in toluene containing 1-methylindole as an internal standard. Separation of the constituents was achieved by injection into a gas chromatograph equipped with a BP1 capillary column (25 m x 0.5mm), a nitrogen specific detector and temperature programmed oven from 30°C to 280°C at 4°C per minute. Peaks from the nitrogen specific detector with a retention time between that for 1-methylindole and carbazole were considered to be alkylindoles with reference to previously published chromatograms⁶. All peaks in this range were summed and converted to a mole concentration by assuming an equal molar response on the nitrogen specific detector to that for 1-methylindole.

RESULTS AND DISCUSSION

The effect of oxygen pressure, temperature and time has previously been reported for the oxygen overpressure (OP) technique.³ Little variation was found when the oxygen pressure exceeded 350 kPa, so all measurements in this study were carried out with an oxygen pressure of 794 kPa (100 psig). With one of the refinery fuel blends in this study (A1), comparative measurements were made between a number of OP conditions and the ASTM D2274 and ASTM D4625 procedures. As may be seen from Table 1, sediment corresponding to medium instability was obtained for the ASTM D2274 and ASTM D4625 procedures for fuel A1. Similar amounts of sediment were obtained from 26 hr/80C and 16 hr/95C OP conditions.

FUEL	ASTM D2274 16 hr 95C mg/L	ASTM D4625 13 weeks 43C mg/L	OXYGEN OVERPRESSURE				
			26 hr 80C mg/L	16 hr 90C mg/L	794 kPa O ₂ 16 hr 95C mg/L	64 hr 95C mg/L	16 hr 120C mg/L
A1	13	18	16	8	18	70	88
F1		15		33		119	

Table 1. Comparison of Total Sediment from ASTM D2274 and ASTM D4625 ageing with oxygen overpressure ageing for fuel A1 and F1.

Less sediment was obtained from 16 hr/90C OP conditions. A smaller number of comparative measurements was made for fuel F1. However, comparing only ASTM D4625 conditions with those for OP at 16 hr/90C, it may be noted that OP conditions produced 2.2 times as much sediment, whereas for fuel A1, the equivalent ratio was 0.4.

The total amount of sediment increased significantly as the temperature or time of ageing increased for OP conditions. The sediments produced by the experiments shown in Table 1 were separated into constituents by thin layer chromatography on silica gel. The results are shown schematically in Table 2.

A high degree of similarity in the species was observed in the sediment produced under ASTM D4625 conditions and OP conditions of 16 hr/90C. There was a higher degree of similarity in these chromatograms than those only for ASTM D4625 conditions from ageing the low and high alkylindole content blends of Table 3. Details of the ASTM D4625 sediments will be discussed elsewhere at this conference⁵ with rate process associated with the formation of the species.⁷

A major feature of the thin layer chromatograms was the increased intensity in the OP 16 hr/90C sediments of the pink material at an R_f value of approximately 0.45 and the orange material at approximate R_f 0.25. The intensity of this orange material was less on freshly chromatographed plates, but increased with age. If the orange band at R_f 0.25 was rechromatographed, an orange band at approximate R_f 0.90 was formed. Rechromatography of the pink material at R_f 0.45 again produced an equivalent pink band, but also an orange material at R_f 0.25. It is postulated that the pink material is the acid salts of indolylphenalenones, which partly disassociate on the thin layer plates to form orange indolylphenalenones.⁸ The increased formation of indolylphenalenone products under OP conditions is consistent with the increased oxidation environment.

The blue material at approximate R_f 0.30 is believed to be acid salts of indolylphenalenes.⁹ These salts are very pronounced in the high alkylindole fuel sediment under ASTM D4625 conditions. The proportion of the blue material decreased as the temperature and time of the OP conditions increased. At the longer OP times (64 hours) and temperatures (120°C), the proportion of brown streaking material on the thin layer chromatograms increased. This material extended over all R_f values and was the predominate material in the chromatogram of the OP 120°C sediments. As the formation of the brown material is accompanied by a decrease in the pink and blue materials on the thin layer chromatograms, it is postulated to be a polymeric material produced by further reaction of the indolylphenalene and indolylphenalenone salts. The formation of the brown material places an upper limit on the temperature of the oxygen overpressure test.

Comparison of the amount of sediment produced by ASTM D4625 conditions and the OP test at 16 hr/90C was extended to 15 fuels blends shown in Table 3. Whereas the ratio of sediment produced by the two procedures is within 1.0 ± 0.2 for a number of fuels, many fuels show a significant deviation from this ratio. No definite trend is obvious from the data in the table. The number of fuels in which significantly more sediment is produced by OP conditions is greater than the number of fuels in which significantly less sediment is produced. This may be the reason that these OP conditions have been postulated to be equivalent to three years ambient storage.³ However, this extrapolation would be very favourable to fuels such as A1 and E2 which produce significantly less sediment under the OP conditions. Attempts to correlate the total amount of alkylindoles in the fuels with agreement of the total amount of sediments by the two procedures did not yield any obvious relationship.

The comparative study was extended to some commercial automotive diesel fuels collected from Northern Australia which had been in storage for 12 months at ambient

temperatures. It may be noted that oxygen overpressure determinations and measurement of alkylindole concentrations were carried out on fuel which had been aged for at least 12 months and from which sediment produced by the ambient ageing had been removed. As may be seen from the data in Table 4, there does not appear to be any relationship between the gravimetric amount of sediment produced by the two procedures. The ratio of sediment produced by one year ambient ageing compared to OP conditions ranged from 0.3 to 2.8.

CONCLUSIONS

The oxygen overpressure test at a temperature of 90°C for 16 hours at 794 kPa pressure oxygen will produce comparable amounts of sediment for many fuels to that formed by ageing the fuel for 13 weeks at 43°C. However, there are a significant number of fuels which either produce greater or smaller amounts of sediment under oxygen overpressure conditions compared to lower temperature air environment ageing. As the difference in the relative amount of sediment is in both directions, it is unlikely that variation of the oxygen overpressure conditions will produce good correlation for all fuels. In this study, an attempt was also made to correlate the variation in relative amount of sediment with the total amount of alkylindoles in the fuel, but no relationship could be found.

Conclusions reached from the use of relative amounts of total sediment produced by oxygen overpressure conditions as the sole reference criteria for mechanistic studies of distillate fuel ageing processes should be interpreted with much caution.

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FUEL A1					
R _f RANGE	BAND COLOUR	ASTM D4625 13 weeks 43C	16 hr 90C	794 kPa O ₂ 64 hr 95C	16 hr 120C
1.00-0.95	green	L	VL	VL	VL
0.92-0.84	orange	L	L	L	M
0.73-0.71	green	VL	VL	VL	VL
0.64-0.62	grey	VL	VL	VL	VL
0.56-0.55	grey	VL	VL	VL	VL
0.49-0.33	pink	M	L	L	NO
0.33-0.25	blue	M	M	VL	VL
0.25-0.19	orange	NO	M	L	NO
0.25-0.19	pink	M	NO	NO	NO
0.09-0.06	brown	M	M	M	D
0.05-0.02	yellow	M	M	M	NO

FUEL F1				
R _f RANGE	BAND COLOUR	ASTM D4625 13 weeks 43C	16 hr 90C	794 kPa O ₂ 64 hr 95C
1.00-0.96	green	L	L	L
0.94-0.87	orange	M	M	M
0.55-0.49	violet	L	L	L
0.49-0.46	pink	L	M	M
0.46-0.27	blue	D	M	L
0.27-0.22	orange	L	M	NO
0.10-0.08	brown	NO	M	D
0.05-0.03	yellow	L	M	VL
	NO	not observed		
	VL	very light		
	L	light		
	M	medium		
	D	dark		

Table 2. Thin layer chromatogram schematics of sediment from fuel A1 (low alkylindoles) and F1 (high alkylindoles).

FUEL SAMPLE	ASTM D4625 mg/L	OXYGEN OVERPRESSURE mg/L	RATIO	TOTAL ALKYLINDOLES* umol/L
A1	17.8	8.0	2.2	384
B1	11.8	19.5	0.6	632
B2	0.4	4.0	0.1	193
C1	19.0	19.9	1.0	506
C2	0.6	<0.1	>6.0	54
D1	9.0	10.0	0.9	nd
D2	0.8	1.0	0.8	nd
E1	56.2	47.0	1.2	1204
E2	7.9	1.0	7.9	nd
F1	14.6	33.2	0.4	1089
F2	18.6	21.3	0.9	904
G1	12.3	11.4	1.1	707
G2	0.2	2.0	0.1	49
FG1	12.4	24.5	0.5	nd
FG2	18.1	19.0	1.0	nd

* Assuming equal molar detector response to 1-methylindole

X1 30% LCO/SRD fuel blends

X2 30% HTLCO/SRD fuel blends

nd not determined

Table 3. Comparison of Total Sediment from ASTM D4625 (13 weeks at 43°C) with oxygen overpressure ageing (16 hours at 90°C with 794 kPa pressure oxygen) for 30% LCO/SRD and 30% HTLCO/SRD fuel blends.

FUEL SAMPLE	COLOUR ASTM D1500	AMBIENT mg/L	OXYGEN OVERPRESSURE mg/L	RATIO	TOTAL ALKYLINDOLES* umol/L
1	2.5	14	43	0.3	355
2	4.0	39	30	0.8	nd
3	1.5	14	16	0.9	44
4	2.0	11	4	2.8	129
5	1.5	11	24	0.5	17
6	1.5	5	5	1.0	<10
7	nd	11	<1	>11	223

* Assuming equal molar response to 1-methylindole

nd not determined

Table 4. Comparison of Total Sediment from one year ageing at ambient temperature with oxygen overpressure ageing (16 hours at 90°C with 794 kPa pressure oxygen) for commercial fuels from Northern Australia.

DEVELOPMENTS IN DIESEL FUEL STABILITY FORECAST METHODS

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ABSTRACT

A rapid oven test was designed and used for estimation of diesel fuel stability forecasts as well as for establishing mechanisms of diesel fuel degradation processes. The 17 hours test at 110°C in specially designed bottles allows withdrawal of a vapour phase sample, enabling determination of the oxygen depletion rate, which, in conjunction with the gum formation rate, indicates whether the degradation process is of an oxidative or a polymerization type. In order to enable determination of gum formation rate in diesel fuels of a final boiling point above 300°C, a special procedure had to be devised. The gum content of any diesel fuel is of a large importance, since it indicates not only the rate of degradation products formation, but also allows its physical examination. The estimates for diesel fuel storage stability properties as used in the Rapid Oven Test (ROT) are existent gum (determined by the modified procedure), oxygen depletion in the vapour phase, acidity and colour, - all before and after exposure to the oven test. The rate of change of these properties indicates the resistivity of the diesel fuel to environmental influences during storage.

THE BACKGROUND

Difficulties have been experienced when diesel fuels had to be evaluated in respect of their behaviour in medium and in long term storage, especially in case of their operational stabilities. Operational stabilities, as referred to in this paper, are associated with the behaviour of diesel fuels in fuel tanks of vehicles or equipment, which have to be ready for immediate use, even when not operated constantly. Such vehicles or equipment are put into operation from time to time in order to ensure their proper functioning. The diesel fuel is thus circulated in the fuel system and exposed to high temperatures and contact with metals before it is returned to the fuel tank. Such conditions are extremely unfavourable to the diesel fuel properties, especially if their chemical composition makes them susceptible to changes in their original properties and to formation of degradation products.

The growing use of catalytic crackers and visbreakers, necessary for production of increased proportions of distillates in general and of motor gasolines in particular, yield correspondingly larger

amounts of cracked (unstable) middle distillates. These can be hydrotreated in order to saturate some of the unsaturated components, thus improving their stabilities, - or they can be used as diluents for back-blending heavy residues for obtaining specification grade residual fuel oils. Stability improving additives can be also used for obtaining satisfactorily stable products. Nevertheless, some of the cracked middle distillates find their way into the diesel fuels, impairing so their stability properties.

The situation described in the foregoing makes it necessary to:

- a. Employ efficient means for estimating stability properties of diesel fuels in short, medium and long term storage, as well as their operational stabilities;
- b. Have at disposal suitable testing procedures for evaluation of stability improving additives, in respect of types as well as of concentrations.

DIESEL FUEL STABILITY ESTIMATING PROCEDURES

Good diesel fuel stability estimates should fulfil the following requirements:

- a. They should be reliably indicative of the diesel fuel stability properties;
- b. The obtained results should be well reproducible;
- c. Testing procedures should be easily and fastly carried out and results should be obtainable after an as short a time as possible.

Most of the the presently used oven tests respond well to the first two conditions, but not to the third, which in itself is of a large importance in routine stability monitoring. An effort was therefore made to devise an accelerated oven test, which would respond to all the above mentioned requirements.

The oven test procedure suggested in this respect is the Rapid Oven Test (ROT), in which fuel samples are kept for 17 hours at a temperature of 110°C in half liter glass bottles, sealed with crimp type caps enabling puncture and withdrawal of vapour samples from the outage with a hypodermic syringe. The main parameters serving as stability estimates are total gums (composed of filterable sediment, adherent insolubles and existent gum), and oxygen depletion in the vapour phase above the tested fuel.

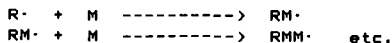
EXISTENT GUM OF WIDE BOILING POINT RANGE DIESEL FUELS

Values of existent gum are indicating the rate of degradation products formation and are therefore of a great importance. Moreover, the physical formation of gums allows the determination of their chemical composition, which in itself is also a valuable tool in the study of degradation products formation in diesel fuels.

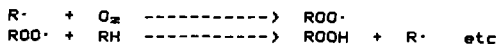
The problem in this respect is that the current method for existent gum determination (ASTM D 381) is suitable only for diesel fuels the final boiling point of which does not exceed 320°C. A modified method allowing existent gum determinations of diesel fuels of a final boiling point of up to 400°C had to be therefore devised. The proposed procedure is based on evaporating a blend consisting of 25% volume of the full range diesel fuel and 75% volume of a kerosine, the existent gum of which had been previously determined and is used as a blank. 50 ml of the blend are evaporated under conditions prescribed by the ASTM D 381 procedure. The residue is weighed and the result is reported as mg gum per 100 ml of the diesel fuel, after the contribution of the kerosine gum (blank) had been deducted.

DETERMINATION OF BREAKDOWN MECHANISMS BY THE RAPID OVEN TEST

The oxygen depletion rates indicate not only the degradation products formation rate but also the nature of the particular degradation process: In case of gum formation without an appreciable drop in the oxygen content of the gaseous phase, the degradation process can be assumed to be of a polymerization nature:



In case the degradation process is accompanied by a significant drop in the oxygen content of the gaseous phase, it can be assumed to be of an oxidative nature. This can be also seen by the peroxides content of the tested fuel or the chemical composition of the gums:



Since these polymerization chain reaction mechanisms are well known, they are not discussed in detail in the framework of this paper.

DISCUSSION OF RESULTS

Table 1 summarizes properties of the four diesel fuel types used in the experimental sets described in this paper:

Type A is a straight run product of a relatively low final boiling point and is assumed to be relatively stable. Types B and C are diesel fuels of wider boiling point ranges, the final boiling point being

about 370°C. Type B is an aged product a sample of which had been drawn from an experimental long term field storage tank, while Type C is a corresponding freshly produced product.

Type D is a blend of the Type C commercial product and a cracked gas oil sample in a ratio of 2 to 1. This diesel fuel sample is assumed to be unstable. The analysis of the cracked gas oil component is given in the last column of Table 1.

Comparative results of long term storage stability tests of the four diesel fuel types, using several testing procedures, are given in Table 2 and Table 3:

Samples were drawn and analysed at the beginning of the storage period and after 14, 25 and 45 weeks of storage at ambient temperature in vented steel drums. Stability tests of each of the samples were carried out according to the particular procedure of each of the test methods and observations as to the following items were recorded:

- a. Comparison of results obtained by the various testing procedures, especially in respect of their correlation with results obtained by the Rapid Oven Test (Table 2);
- b. Effect of the long term storage period on the results obtained by the various testing procedures (Table 2);
- c. Effect of the diesel fuel characteristics on results obtained by the various testing procedures (Table 2);
- d. Evaluation of stability improving additives added to the various diesel fuel types, before, during and after long term storage, - using several stability test methods (Table 3).

a. Comparison of results obtained by the various testing procedures:

It is not always possible to compare absolute results obtained by the various stability tests: For example peroxide contents or gum formation rates in samples subjected to accelerated oxidations or to U.V. irradiations are higher than those obtained by the Rapid Oven Test, but peroxide contents and gums obtained by the Rapid Oven Test are higher than those obtained by other oven tests, in which contact with air is limited. Trends, rather than absolute results, should be therefore taken into consideration. Examination of these trends indicates a satisfactory correlation between the stability testing procedures used in this context.

It was observed that for diesel fuels containing stability improving additives, some of the obtained results were rather erratic. This is especially true in cases where unsuitable additives had been used or when their concentrations were either insufficient or excessive. This

phenomena can be explained by the susceptibility of some of the additives to the severity of some of the testing procedures, affecting the obtained results correspondingly. In this case oven storage tests, rather than accelerated oxidations or U.V. irradiations, should be used preferably. The Rapid Oven Test, being less time consuming, is especially suitable in this case.

b. Effect of long term storage:

Degradation formation rates are affected by exposure of diesel fuel samples to long term storage. It is interesting to note that Type B diesel fuel (taken from an experimental field storage tank, i.e. an aged sample) exhibits much higher degradation product formation rates than a corresponding fresh product (Type C); this is true before, as well as during the laboratory storage. All the stability testing procedures used show the same trend.

c. Effect of diesel fuel characteristics:

Fresh straight run diesel fuel samples (Type A and Type C) are less affected by long term storage as compared to the aged diesel fuel sample (Type B); the most affected sample during storage is the diesel fuel containing a cracked gas oil component (Type D). This trend can be seen by all the procedures used in this respect.

d. Evaluation of stability improving additives:

From the many data obtained in several experimental sets carried out in this respect, it can be seen that the type as well as the concentration of the stability improving additives has to be determined in each case. Some additives are suitable for one type of diesel fuels, while not improving the situation in case of another type. Concentrations of stability improving additives have also to be adjusted according to the diesel fuel type. Unsuitable additives, or insufficient or excessive concentrations, might affect the degradation product formation rate adversely.

It should be remarked that for brevity sake not all the results discussed in the foregoing are reported in this paper; however, the foregoing discussion is based on numerous data obtained in several experimental sets.

CONCLUSIONS

The proposed Rapid Oven Test has been described and compared to other diesel fuel stability testing procedures and satisfactory correlation has been established. The merits of this test have been discussed as follows: Results obtained by the ROT are usually well reproducible and indicative as to the stability properties of diesel fuels; as an oven test the ROT is not excessively time consuming and yields results in an acceptable period of time; the ROT enables drawing of conclusions as to breakdown mechanism for each particular case and finally, results obtained by the ROT are less erratic in case of diesel fuels containing less suitable additives especially if those are added at insufficient or excessive concentrations.

TABLE 1: Analyses of diesel fuel types used for evaluation of stability testing procedures

Test Method	Unit	R e s u l t s				
		Light Atmospheric Gas Oil (TYPE A)	Gas Oil from Field Storage (TYPE B)	Commercial Gas Oil (TYPE C)	Comm. G. Oil - Bleed 2:1 (TYPE D)	Cracked Gas Oil
Density, 15°C, ASTM D-1298	gr/cm ³	0.8442	0.8544	0.8512	0.8696	0.9058
Boiling Range ASTM D-2887	°C	218-327	208-370	220-368	198-362	197-298
Refractivity Index ASTM D-1218		1.46805	1.4730	1.47205	1.48605	-
Pour Point ASTM D-97	°C	-15	0	0	-6	<-30
Cloud Point ASTM D-2500	°C	-14	+3	+3	-4	<-30
Cold Filter Plugging Point IP-309	°C	-15	+2	0	-5	<-30
ndM Analysis						
Aromatic Rings		0.28	0.53	0.53	0.8	-
Naphthenic Rings		0.93	0.56	0.56	0.31	-
C in Aromatic Structure	%	11.4	19	19	32.9	-
C in Naphthenic Structure	%	37.2	20	20	16.7	-
C in Paraffinic Structure	%	51.2	61	61	50.3	-
Aniline Point IP-2	°C	70.1	72.4	72.4	55.2	<30
Bromine Number IP-129		0.6	0.6	0.7	3.9	10
Carbon Residue (Conradson) ASTM D-189	% mass	0.04	0.01	0.03	0.05	0.55
Total Sulphur Content ASTM D-129	% mass	0.42	0.52	0.53	1.05	-
Basic Nitrogen Content IUP-384	ppm	770	770	250	210	-
Basic Nitrogen IUP-269	ppm	67	120	59	69	93
Pyrololes IUP-276	ppm	1.5	1	1.5	1	-
Filterable Insolubles ASTM D-2276 (mod.)	mg/liter	0.4	1	2	2	-
Existent Gum ASTM D-381 (mod.)	mg/100 ml	<1	<1	<1	3	17
Peroxides ASTM D-3703 (mod.)	meq/liter	0.7	1.8	0.4	0.9	-
Acidity ASTM D-974	mg KOH/gr	0.03	0.008	0.03	0.03	0.01
Color ASTM D-1500		0.5	2	1	2.5	4

TABLE 2: Long term storage stabilities of diesel fuels without additives

	TYPE A			TYPE B			TYPE C			TYPE D		
	Car oil before storage	After 14 weeks storage	After 25 weeks storage	After 45 weeks storage	Car oil before storage	After 14 weeks storage	After 25 weeks storage	After 45 weeks storage	Car oil before storage	After 14 weeks storage	After 25 weeks storage	After 45 weeks storage
Carbon Residue, % mass	0.05	0.06	0.04	0.05	0.01	0.05	0.02	0.09	0.03	0.05	0.01	0.06
Filterable Insolubles, mg/100 ml	0.04	0.26	0.5	0.6*	0.1	0.4	0.2	22.3*	0.2	0.2	0.3	4.2*
Existent Gum, mg/100 ml	0	1.2	1.6	1.8	1	2.6	1.4	7.6	<1	0.4	0	3.8
Peroxide Content, mg/l	0.73	0.12	0.14	0.7	1.8	0.8	1.4	3.9	0.033	0.16	0	0.23
Acidity, mg KOH/gr	0.03	0.03	0.03	0.77	0.01	0.1	0.006	0.13	0.033	0.04	0.03	0.29
Colour Union	<0.5	<0.5	1	1.5	<2	<3	4	4	<1	<1.5	1.5	1.5
ACCELERATED OXIDATION ASTM D-274												
Peroxide Content, mg/l	-	0.65	2.9	2.1	-	1.7	1.3	2.3	-	0.4	1.5	0.5
Colour Union	-	-	3	3	-	-	-	5	-	-	-	3
Adherent Insolubles, mg/100 ml	0.1	0.8	0.6	0.6	1.5	0.3	0.8	0.3	0.1	0.2	1	0.1
Filterable Sediment, mg/100 ml	0.3	1.1	0.7	0.7	0.4	0.6	0.7	0.2	0.2	0.4	0.3	0.6
Total Sediment (ash), mg/100 ml	0.4	3.9	3.3	3.3	1.9	0.9	1.0	0.5	0.3	0.6	1.3	0.7
Existent Gum, mg/100 ml	-	3.2	6.7	5.8	-	2.9	3.6	4	-	8.1	8.3	2.4
UV IRRADIATION												
Peroxide Content, mg/l	0.73	0.53	0.38	2	1.8	1.3	2.7	2.35	0.4	0.8	0.9	0.94
Colour Union	<0.5	<0.5	1	2	<2	<3	4.5	4.5	<1	<1.5	2.5	2
Existent Gum, mg/100 ml	1.4	1.2	4.4	4	2.8	6.6	5.4	16.8	4.4	1.2	3.6	5.6
RAPID OVEN TEST												
Oxygen Consumption, %	-	10	4.8	8.6	9	8	5	10.5	2	-	1	5.3
Peroxide Content, mg/l	-	-	1.4	-	-	-	2.6	-	-	-	1.3	-
Colour Union	-	-	-	3	-	-	-	5	-	-	-	2.5
Filterable Sediment, mg/100 ml	0.5	0.92	1	1.3	2.2	0.7	1.5	0.9	0.2	0.3	1.7	0.7
Adherent Insolubles, mg/100 ml	0.2	1.5	0.8	2.2	0.3	0.2	0.6	1.3	0.5	1.0	0.5	0.4
Existent Gum, mg/100 ml	2.7	2.1	5.2	3.9	2.8	6.2	6.3	11.3	2.9	1.9	6.5	4
Total Gums (a+b+c)	3.4	4.5	7	7.4	5.3	7.1	3.4	13.5	3.6	3.7	8.7	5.1
BURNOUT 150°C TEST												
Colour Union (before)	<0.5	<0.5	1	1.5	<2	<3	4	4	<1	-	1.5	1.5
Colour Union (after)	<1	<1	2	2.5	<3	<3.5	4.5	5.5	<1.5	-	2	2
Base of the Blotter	3	4	3	3	5	7	8	8	-	-	2	4
Filterable Sediment, mg/100 ml	-	-	0	-	-	3.7	-	-	-	-	0.4	-
Peroxide Content, mg/l	-	-	0.3	1.2	-	-	2.1	1.6	-	-	0.3	0

*after

TABLE 3 : Long term storage stabilities of diesel fuels with 80 ppm Additive B

	Type A			Type B			Type C			Type D		
	Gas oil before storage	After 25 weeks storage	After 45 weeks storage	Gas oil before storage	After 25 weeks storage	After 45 weeks storage	Gas oil before storage	After 25 weeks storage	After 45 weeks storage	Gas oil before storage	After 25 weeks storage	After 45 weeks storage
Carbon Residue, % mass	0.02	0.08	0.03	0.03	0.02	0.05	0.02	0.03	0.04	0.06	0.03	0.13
Filterable Insolubles, mg/100 ml	2	0.68	0.43	0.3	0.62	0.36	0.7	0.4	0.56	1.4	0.95	1.9
Existent Gum, mg/100 ml	2.8	1.0	1.6	5.7	12.8	5.8	1.8	1.8	3.8	3.5	7.0	10.6
Peroxides Content, meq/l	0	0.36	0	0	1.6	0	0	0	0	0.05	1.2	0
Acidity, mg KOH/gr	0.03	0.1	0.04	0.02	0.04	0.03	0.03	0.08	0.04	0.03	0.06	0.03
Colour Union	<1	<1.5	1	<3	3.5	3.5	<1.5	1.5	1.5	<3.5	4	4.5
AFTER ACCELERATED OXIDATION												
ASTM D-2274												
Peroxide Content, meq/l	0.05	0.7	-	2	1.4	-	0.05	0	-	1.4	2.4	-
Colour Union	-	1.5	-	-	4.0	-	-	2.0	-	-	5.0	-
Adherent Insolubles, mg/100 ml	0.4	0.3	0.46	0.2	0.2	0.30	0.13	0.12	0.2	0.7	0.5	0.62
Filterable Sediment, mg/100 ml	0.2	0.14	0.16	0.7	0.07	0.28	0.24	0.31	0.2	0.6	1.04	0.90
Total Sediment (a+b), mg/100 ml	0.6	0.44	0.62	0.9	0.27	0.58	0.37	0.43	0.4	1.3	1.6	1.52
Existent Gum, mg/100 ml	4	2.1	-	3	6	-	3.6	5.6	-	12.5	12.8	-
UV STABILIZATION												
Oxygen Consumption, %	0.05	1.6	0	1.8	1.6	0	0.005	0.47	0	1.2	2.1	0
Peroxides Content, meq/l	<1	1.5	3	<3	3.5	3.5	<1.5	2.0	1.5	<4	4.5	4.5
Colour Union	0.4	0.6	1.6	2.6	14.4	18.4	0.7	4.2	4.2	5.8	8.8	13.8
R.O.T.												
Oxygen Consumption, %	-	1.4	2.1	-	2.6	3.3	-	2	3.8	4.8	6.7	11.9
Peroxides Content, meq/l	0.03	-	0	1.8	-	0	0.2	-	0	1.3	-	tracts
Colour Union	-	2	-	-	4.5	-	-	2.5	-	-	3.5	-
Filterable Sediment, mg/100 ml	0.2	0.2	0.4	0	0.04	0.4	0.2	0.2	8	1.5	3.7	5.2
Adherent Insolubles, mg/100 ml	0.2	1.8	0.4	0	0.07	0.2	0	0.3	0	0.4	3.6	0
Existent Gum, mg/100 ml	1.4	4.2	3.4	4	5	7.2	0.6	4	-	7.9	21.8	-
Total Gums (a+b+c)	1.8	6.2	4.2	4	5.1	7.8	0.8	4.5	-	9.8	29.1	-

THE USE OF SIMPLE RAPID COLORIMETRIC TECHNIQUES FOR MEASUREMENT OF LIGHT CYCLE OIL CONTENT AND RELATIVE STORAGE STABILITY OF DISTILLATE FUELS

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ABSTRACT A simple colorimetric technique has been developed which accurately measures the relative amount of unhydrogenated light cycle oil in distillate fuels. Distinctive colours are formed within 10 minutes from the addition of 1 - 2 ml of fuel to a small column of active white powder in clear glass or plastic tubes. Visually, the intensity and colouration of the powder may be immediately correlated with the type and amount of light cycle oil in the fuel. Analytical values with higher degrees of precision for light cycle oil contents in the 0 to 30% range are obtained by washing the coloured material from the tubes with solvent and measuring the absorbance with a colorimeter or spectrophotometer. Results are presented for the correlation between colorimetric values, unhydrogenated light cycle oil content and diesel fuel storage stability.

INTRODUCTION

Many studies have implicated polar compounds of oxygen,^{1,2} nitrogen³ and sulphur⁴ in hydrocarbon fuel mixtures for the degradation of hydrocarbon fuels upon storage. However, although many mechanisms have been postulated, none of these processes will fully explain the nature of the sediment formed by degradation of automotive diesel fuel.⁵

Better understanding of the chemistry of diesel fuel degradation will not only allow development of rapid and accurate tests for the measurement of fuel instability, but also modification of refinery processes to minimize the formation of detrimental species. The presence of unhydrogenated middle distillate light cycle oil from cracking of heavier petroleum components plays a significant role in the degradation of automotive diesel fuel.⁶

Rates of possible processes occurring in automotive diesel fuel containing light cycle oil have been investigated towards understanding the chemistry of fuel degradation.⁷ Variations in absorbance in both the ultraviolet and visible regions were used to measure rates of reaction.⁸ The colour of species which absorb in the visible region of the spectrum can be detected by eye. In this paper, the use of visual and instrumental absorption procedures are presented to illustrate the ease with which light cycle oil can be detected by direct means in as little as 0.5 ml of automotive diesel fuel.

EXPERIMENTAL

Reference fuels used in this study were samples from automotive distillate refinery streams of straight run distillate (SRD), light cycle oil (LCO) and hydrotreated light cycle oil (HTLCO) obtained directly from Australian refineries within one week of production. Samples were either blended immediately for ageing studies or stored as unblended components at -12°C. Experimental blends were prepared by mixing on a volumetric basis freshly thawed

LCO or HTLCO with SRD. Ten commercial automotive diesel fuels purchased directly from retail outlets were also included in this study.

The LCO Colorimetric Tubes were prototype units developed at the Materials Research Laboratory of the Defence Science and Technology Organization. Results obtained in this study were obtained with 4 cm of active white powdered solid material packed in 5 mm diameter glass tubes. It is anticipated that standardized Colorimetric Tubes will be produced commercially in unbreakable clear plastic packs under licence to the Commonwealth of Australia.

Plastic syringes were used to add 2 ml of fuel to the Colorimetric Tubes and apply gentle pressure so that the fuel passed through the column of powdered material in the tubes within 30 seconds. Colour development commenced immediately on the white powder and in most cases full visual development was achieved at ambient temperatures within 10 minutes. Spectral measurements reported in this paper were obtained after washing the column with 1 ml of hexane to remove residual fuel followed by 6 ml of methanol. In each case, gentle pressure was applied from the syringe used to add the liquid so that it passed through the powdered solid within 30 seconds. Spectra were recorded immediately in the methanol wash liquid using 1 cm pathlength cells.

Comparative ageing studies were done at 43°C for 13 weeks by the method of ASTM D4625 or by an oxygen overpressure technique at 90°C.⁹ The single bomb apparatus of ASTM D942 was used for the oxygen overpressure measurements as described elsewhere.¹⁰

RESULTS AND DISCUSSIONS

Results reported in this presentation represent colorimetric development which was the composite of a large number of chemical processes from which possible reactions may be postulated.⁸ The active solid powder was a mixture of a number of possible ingredients which may be formulated with a large range of activities and selectivities. The white powder acts both as an active catalyst and solid support for colour development.

Visual colour development was rapid (within 5 minutes) and occurred in contact with very small amounts of unhydrogenated LCO. One batch of active powder had to be discarded after being coloured by accidental contact with a stirring rod which was unwashed after being used to stir a blend of LCO. The normal human eye is very sensitive to differentiating comparative shades of colour which are difficult to reproduce in coloured photography and not feasible in a black and white conference proceedings. Maximum selectivity to visual observations for a range of LCO concentrations was obtained by using an active powder with low catalytic activity. Coloured slides of Colorimetric Tubes forming part of the in-session presentation are from tubes with low catalytic activity.

Medium to high catalytic activity promotes more rapid colour development (no further noticeable visual changes after one minute) and a final colour which was black or a very dark blue/green. The visual colour variation was greatly reduced for a range of LCO from 0 to 30%. However, if coloured material was washed from the active powder as described in the experimental section, a variation in the absorbance was readily seen as determined by a simple colorimeter or a spectrophotometer.

The rapidity of the colour development is shown in Figure 1, in which the Colorimetric Tubes of medium catalytic activity were washed after 2 to 1500 minutes following the addition of 2 ml of fuel containing 15% LCO oil from refinery F (refinery designations as in other presentations at this conference¹¹). Both the absorbance and the peak maximum were a function of time. However, from 300 to 1400 minutes the absorbance at 650 nm was relatively constant. This follows from the broad band absorbance in the region 600 - 700 nm which is

shown in Figure 2 for the fuel after 300 minutes contact time with the active powder in the Colorimetric Tube.

Following from Figures 1 and 2, it was concluded that the most consistent results would be obtained by allowing fuel material to stand on the Colorimetric Tubes for 16 hours (overnight) at ambient temperatures. After the coloured material was washed from the tubes, the absorbance was recorded at the maximum in the region 600 - 700 nm.

Results obtained with 5 blends of LCO from three refineries are shown in Figure 3. The variation of the absorbance with concentration was approximately linear from 0 to 30% LCO content. Refineries A and G were processing Australian Bass Strait crude at the time the samples were obtained, whereas refinery F was processing Middle Eastern crude. It may be noted that the absorbance for a constant LCO content from refinery F was approximately twice that from refineries A and G. It was of interest to compare the amount of sediment produced both by ASTM D4625 and oxygen overpressure ageing as shown in Table 1.

FUEL SAMPLE	ASTM D4625 mg/L	OXYGEN OVERPRESSURE mg/L
A	18	8
F	15	33
G	12	11

Table 1. Sediment produced by ageing 30% LCO in the SRD for 13 weeks at 43°C under ASTM D4625 conditions or 16 hours at 90°C under 794 kPa oxygen overpressure conditions.

Fuel from refinery F which produces the greatest absorbance from the Colorimetric Tubes, produces the most sediment from the oxygen overpressure ageing, but not from the 43°C ageing. The absorbance produced by the fuel mixtures from refineries A and G was very similar, whereas there was a small variation in the amount of sediments produced by the two ageing procedures.

Whereas approximately linear correlation was obtained between the amount of absorbance from Colorimetric Tubes and light cycle oil content (Figure 3), the amount of insoluble sediment produced by increasing LCO content was not linear as shown in Table 2.

It was most probable that chemical reactions producing soluble precursors to insoluble particulate matter increase with increasing LCO content. LCO has a much higher aromatic content (50-80%) than SRD (10-20%) and is a much better solvent than SRD for the insoluble particulate matter. Thus less insoluble matter precipitates from solution. However, the particulate precursors remain in solution where they have an increased tendency to form injector and possibly cylinder deposits. Thus for measurement of LCO content and possible injector deposit potential, the Colorimetric Tubes offer higher precision than gravimetric measurements of deposit formation on ageing.

LCO %	TOTAL SEDIMENT mg/L
5	11
10	20
15	28
20	29
30	33

Table 2. Sediment produced by ageing LCO/SRD blends from refinery F under oxygen overpressure conditions of 794 kPa oxygen at 90°C for 16 hours.

A number of Australian retail automotive diesel fuels have been tested with the Colorimetric Tubes. The absorbance produced after passing 10 retail fuels through Colorimetric Tubes of low activity is shown in Figure 4. Reference fuels are 0 and 1% LCO from refinery G and 5% LCO from refineries A and G. Low activity tubes were used so that visual selection of LCO content could be compared with that obtained by absorbance measurements. As may be seen from the coloured slide projection prepared for oral presentation of this paper, visually fuel 2 is readily selected as producing the darkest blue/green colouration, comparable to that produced by the 5% LCO standards. Fuels 3, 7 and 6 follow in colour intensity of the tubes. Fuel 9 was readily selected as having the least blue/green colour development of the Colorimetric Tubes.

Fuels 2 and 9 were subject to oxygen overpressure ageing at 794 kPa pressure for 64 hours at 95°C. Although this accelerated ageing might be compared to 3-5 years ambient ageing,⁹ only 12 and 1 mg/L of insoluble sediment was produced, consistent with the low and very low levels of unhydrogenated LCO respectively in the fuels.

Undiluted hydrotreated LCO was also passed through the Colorimetric Tubes. That from refineries C and D (reference 10) produced very little colour development, whereas that from refineries E and F produced medium and intense colour development respectively. These results are comparable with sediment levels from 13 weeks 43°C ageing of 30% hydrotreated LCO/SRD blends of less than 1 mg/L from refineries C and D and 8 and 19 mg/L from refineries E and F. It was concluded that either the hydrotreatment process producing the sample at refinery F was ineffective or the sample was unrepresentative.

CONCLUSIONS

Colorimetric tubes have been shown to be a rapid and simple means of determining the amount of unhydrogenated LCO middle distillate fuels either by direct visual means or more quantitatively by colorimetric or spectrophotometric measurements. They are non-toxic and relatively inexpensive to produce and may be used by non-technical personnel in a field environment to obtain direct measurements of relative unhydrogenated light cycle oil content of hydrocarbon fuels. With 2 ml of fuel or less, measurements may be obtained within 10 minutes.

The colour formation on the tubes has been shown to be proportional to both the type of unhydrogenated LCO and the amount in a fuel. The amount and type of LCO may then be

correlated with the formation of sediments by ambient or accelerated ageing techniques. The rapidity and simplicity of the technique makes it ideal for use as a quality control technique at all points of the distribution system, from the refinery outlet, bulk distribution terminal through to the consumer holding tanks. They may be used with any fuel for which control of unhydrogenated LCO is considered desirable. This is primarily the higher quality diesel fuel market at the moment, but the sensitivity of the technique lends itself to determining the effectiveness of hydrogenation for hydrogenated LCO added to aviation distillate.

The Colorimetric Tubes accelerate the rate of reactions of species associated with LCO in small amounts of fuel and concentrate the products in a form which is readily measured. Their use with a wide range of fuels has much potential to enable comparison of the species present in the fuels and a wider understanding of the chemistry associated with fuel instability.

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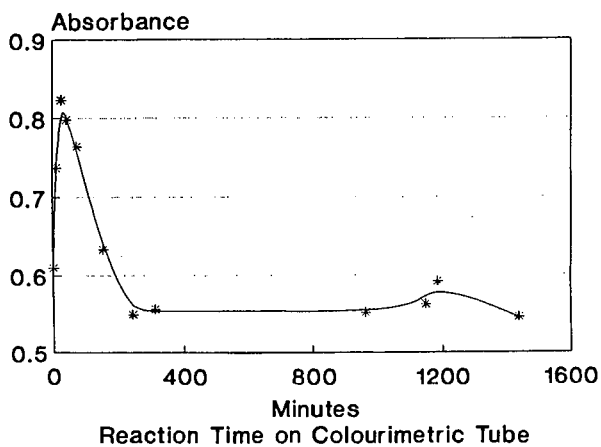


Figure 1. Variation of absorbance at 650 nm of Colorimetric Tube methanol washings for 15% LCO/SRD mixtures of Fuel F.

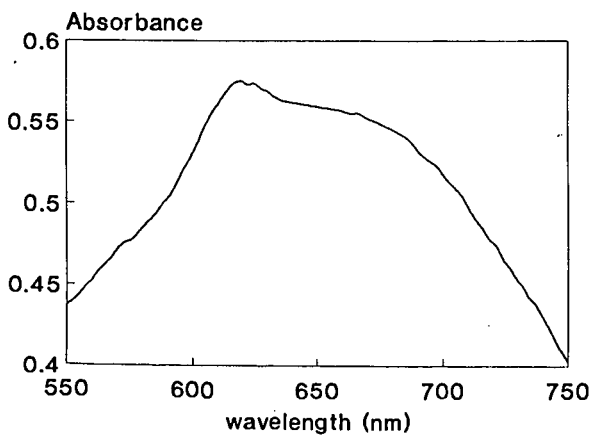


Figure 2. Spectra of Colorimetric Tube methanol washing after 300 minutes reaction time on tube for Fuel F.

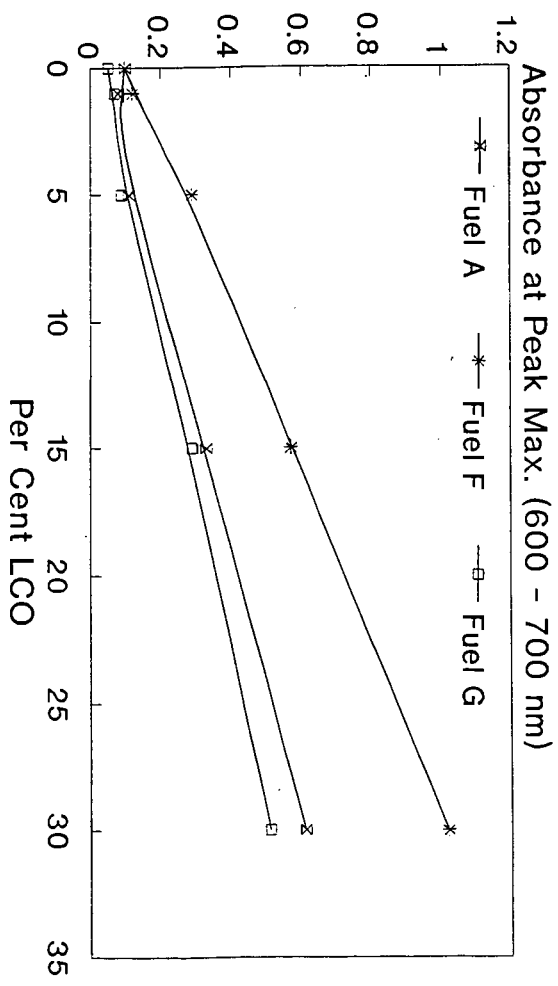


Figure 3. Absorbance of medium activity Colorimetric Tube methanol washings after 16 hours reaction time on the tube at ambient temperatures for Fuels A, F and G.

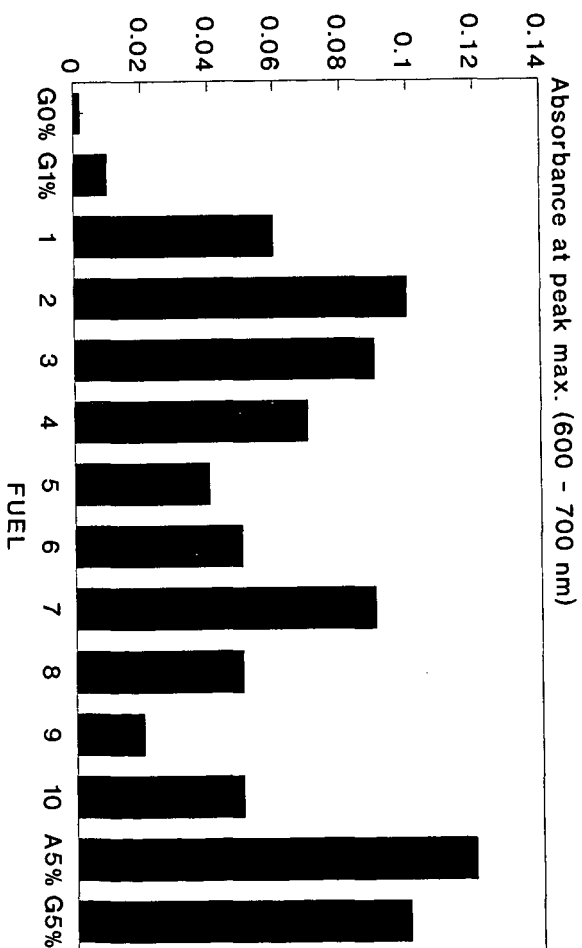


Figure 4. Absorbance of low activity Colorimetric Tube methanol washings after 16 hours reaction time on the tube for 10 commercial automotive diesel fuels compared to 0, 1 and 5% LCO/SRD standards for Fuels A and G.